

Synthesis of graphene oxide with an almost intact carbon framework - a precursor for graphene and an entry to functionalized graphene derivatives

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Abstract

Graphene, a single layer of graphite, has created a completely new interdisciplinary research field.^[1-3] Chemists of all disciplines, physicists and materials scientists constantly recognize new fascinating properties of graphene and its derivatives.

Nevertheless, graphene must become available on large-scale for realizing applications.^[2] Graphene oxide (GO) has a long history and can be produced in large quantities and provides access to individual layers of carbon.^[4] However, the honeycomb lattice generally degrades under the harsh conditions applied for synthesis.^[5, 6] However, several methods are described in the literature, none reaching the quality of graphene prepared by alternative routes like chemical vapor deposition.^[7] Our work intends to increase the understanding of the chemical reactivity of functionalized graphene derivatives. A better understanding is crucial to benefit of the full potential of graphene.

Here, we present a wet-chemical synthetic method that allows for the synthesis of a type of GO whose carbon framework remains almost intact (ai-GO) after oxidation of graphite.^[8] This means that the honeycomb lattice is not damaged severely by the oxidative functionalization procedure. After chemical reduction by hydriodic acid, the graphene is of high quality, which means that the residual defect density is as low as 0.01%.^[9] Statistical Raman microscopy was used to systematically characterize the quality of samples. Furthermore, we prepared transport devices of ai-GO. Therefore, we applied the Langmuir-Blodgett technique to deposit ai-GO flakes onto SiO₂/Si substrates followed by chemical reduction. We identified flakes of high quality by Raman spectroscopy (I_D/I_G ratio < 1) and used electron-beam lithography to pattern Hall bars of those flakes. The Hall mobility measurements we conducted in magnetic fields up to 14 T and temperatures down to 0.3 K.^[8] For the best quality of flakes we identified samples of graphene with a mobility of charge carriers up to 2000 cm²/Vs. This is the highest mobility ever measured using any GO as precursor for the preparation of graphene. Furthermore, we conducted high resolution transmission electron microscopy on ai-GO and can visualize the almost intact carbon framework for the first time. The results confirm that GO with an almost intact carbon framework can be successfully prepared by preventing CO₂ formation during synthesis. Hence, our ai-GO reflects a type of chemically functionalized graphene, since there is a low amount of σ -defects..

With this material in hand we evaluated the stability of the carbon framework by statistical Raman microscopy for the very first time. We investigated the thermal stability of the carbon framework of ai-GO and found that it remains stable up to 100 °C in contrast to conventionally prepared GO.^[10] Functional groups are thermally less stable than the carbon framework. Consequently, one has to discriminate between the stability of functional groups and the stability of the carbon framework. Conclusions about the integrity of the carbon framework in graphene oxide are possible after reduction using scanning Raman spectroscopy. In addition the visualization of the heterogeneity of samples is possible by combining scanning Raman and atomic force microscopy that we additionally correlated with atomic force microscopy. Using this method we were able to compare and determine the efficiency of different reducing agents for ai-GO.^[9]

Furthermore, we evaluated the chemical structure of GO that was prepared in sulfuric acid using an oxidant. Our investigations reveal that organosulfate groups are chemically bound and their amount

approaches one organosulfate group on about 30 carbon atoms^[11]. These organosulfate groups can explain the acidity of graphene oxide that bears an almost intact carbon framework.

Moreover, we could demonstrate that the carbon framework is stable enough to enable chemical reactions, e. g., with sodium hydroxide without degradation of the carbon framework.^[12] This is possible only under certain reaction conditions, while others result in degradation. These findings are a prerequisite to make controlled chemistry with ai-GO. Thus, we used organosulfate groups as a leaving group to introduce anionic nucleophiles, like azide groups above and below the basal plane for the first time.^[13] Establishing this type of reaction represents the ability to functionalize ai-GO with more complex organic structures to fine tune the properties of functionalized graphene.

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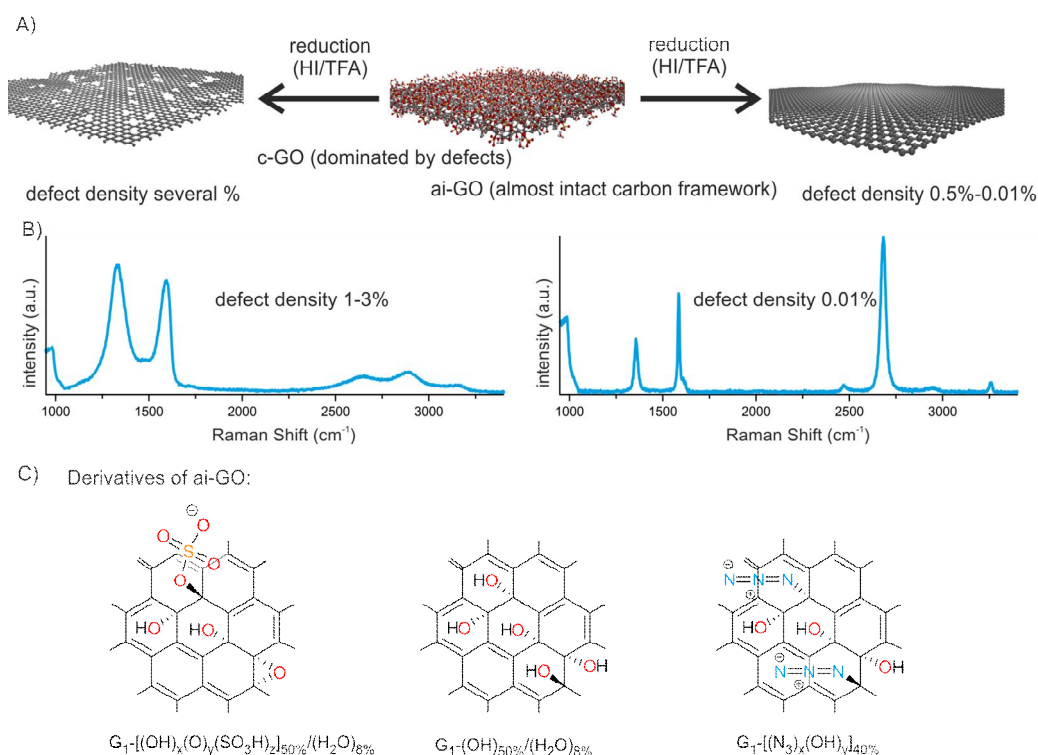


Figure 1. A) Illustration of graphene with defects and without defects; B) Raman spectra of defective graphene and graphene of high quality; C) derivatives of ai-GO with different chemical structures.