Step-wise reduction of immobilized monolayer graphene oxides

Søren Vermehren Petersen, 1 Yudong He, 2 Jiang Lang, 2 Filippo Pizzocchero, 3 Nicolas Bovet, 1 Peter Bøggild, 1 Wenping Hu, 2 and Bo W. Laursen 1

1 Nano-Science Center & Department of Chemistry, University of Copenhagen, Copenhagen, Denmark
2 Institute of Chemistry, Chinese Academy of Science, Beijing, China
3 DTU Nanotech, Technical University of Denmark, Lyngby, Denmark

soerenp@nano.ku.dk

Abstract Chemically converted graphene is highly relevant for transparent conducting film applications such as display and photovoltaic applications [1]. So far, the major obstacle for realizing the potential has been to fully reduce/deoxygenate the graphene oxide (GO), which is challenging in part due to the pronounced aggregation that accompanies deoxygenation of GO in solution [2]. Surface immobilization of monolayered graphene oxide (mGO) in Langmuir-Blodgett (LB) films was investigated as a method to circumvent this problem [3]. Two types of LB films with different density of mGO flakes where prepared, i.e. diluted and coherent, and efficiently deoxygenated in a three-step reduction procedure involving subsequent treatment with hydrazine in dimethylformamide (DMF) to give rGO1, sulfuric acid to give rGO2, and high temperature annealing to give rGO3. The stepwise reduction process was evaluated with optical microscopy, Raman microscopy, and X-ray photoelectron spectroscopy (XPS) along with electrical characterization. XPS measurements confirmed a full conversion into virtually oxygen free chemically converted graphene. The electrical characterization revealed large variations in the conductivity for single sheets in the diluted LB films, with an average conductivity of 100 S/cm. A similar conductivity was found for macroscopic devices made from the coherent LB films with overlapping mGO sheets. The large variation in single sheets conductance is assigned to over-oxidation of the GO leading to formation of holes, which cannot be recovered in the chemical reduction procedure. The study show that the applied three-step reduction procedure is chemically complete and that the conductivity of this chemically converted graphene is limited by structural defects/holes rather than remaining oxygen functionalities.

References


Figures

Figure 1 Deposition and reduction scheme. After GO synthesis and purification, the as prepared mGO films were deposited on Si/SiO2 wafers by LB transfer. After LB deposition, the mGO films were reduced with excess hydrazine, yielding rGO1. The films were then treated with sulfuric acid to obtain rGO2. To obtain the final product rGO3 the films were annealed at high temperature in a reducing atmosphere. As reference samples, both mGO, LB, and rGO1 films were annealed at similar conditions to give a-mGO and a-rGO1, respectively.
Figure 2 Illustration of single sheet and coherent film devices. (A) Device with a single monolayered rGO. (B) Device fabricated from an overlapping rGO3 LB film. The ribbon was scratched out with the micro needles.

Figure 3 Measured conductivities. The red triangles represent average single sheet conductivities for different sample types. The upper and lower bars are the maximum and minimum measurements respectively. The values of the single sheet measurements varied a factor of 10-20. The blue triangle represents the average conductivity for the coherent LB film of rGO3. The upper and lower bars vanish for the coherent film due to coincidence with the triangle.