Two-step graphitization affords full repair of defects in reduced graphene oxide films

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Abstract

Graphene obtained through the so-called graphite oxide route (i.e., reduced graphene oxide) contains a significant number of defects and residual oxygen functionalities that severely degrade many of their properties, such as the electrical conductivity.
Despite efforts to achieve full restoration of the perfect carbon lattice in this type of graphene, such a goal has so far remained elusive by using the implemented reduction approaches and some alternative strategies.

Here, we demonstrate the complete restoration of the carbon lattice in chemically reduced graphene oxide sheets assembled into free-standing, paper-like films through a graphitization approach (i.e., high temperature annealing). By means of a carefully designed heat treatment protocol and extensive characterization of the films by Raman spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction and scanning tunneling microscopy (Fig. 1) we conclude that there are two main stages in the transformation of the films during their graphitization:

(i) full removal of residual oxygen functional groups from the chemically reduced graphene oxide sheets and ensuing generation of atomic vacancies (first annealing step, temperatures of 1500 ^{o}C)
(ii) annihilation of the atomic vacancies and coalescence of adjacent overlapping sheets to form continuous polycrystalline layers in the film (second annealing step, temperatures between 1800 and 2700 ^{o}C).

For the highly graphitized films, the individual domains in the polycrystalline layers exhibit long-range graphitic order, are free of even point defects and their size is mainly determined by the dimensions of the starting reduced graphene oxide sheets (a few to several hundred nanometers). The prevailing type of defect in the polycrystalline layers are thus the grain boundaries separating neighboring domains. These films exhibit electrical conductivity values as high as 577,000 S m^{-1}, which are about 1-2 orders of magnitude larger than those typical of graphene oxide films reduced by chemical or other means.

References

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Figures

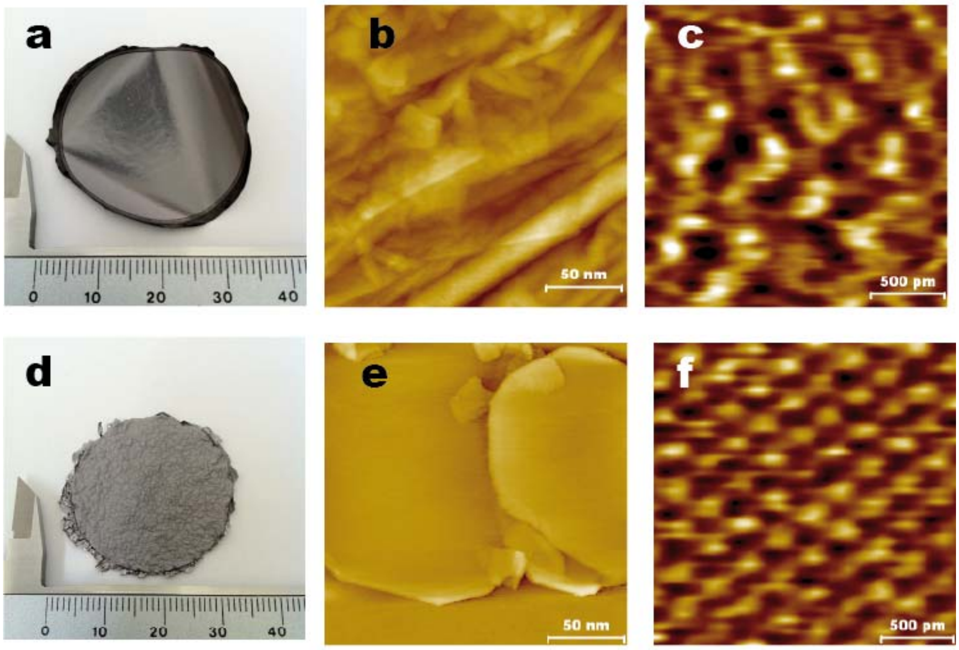

Figure 1: (a-c) Starting free-standing, paper-like film. (d-f). Free-standing, paper-like film first annealed at 1500 ^{o}C and then annealed again at 2700 ^{o}C. (a,b) Digital photographs. (b,e) Nanometer scale STM images. Typical tunneling parameters: 100-300 pA (tunneling current) and 1500 mV (bias voltage). (c,f) Atomic-scale STM images. Typical tunneling parameters: 1-2 nA (tunneling current) and 5-100 mV (bias voltage).