

Functional Groups in Brodie Graphite Oxide: Experimental and DFT study

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Abstract

Graphite oxide (GO) is a non-stoichiometric material with a layered structure obtained by strong oxidation of graphite through the Brodie or Hammers methods, and is an indispensable intermediate product in the most common methods for preparing graphene [1]. In the known structural models of GO, the surface functionality is believed to be composed of hydroxyl, epoxy, and carboxyl groups and, less commonly, also quinoid groups directly bound to graphene layers. However, GO is known to exhibit features such as high oxidative strength and explosive decomposition at 150-200 °C, which cannot be explained if only those functional groups are considered [2].

In this work we synthesized GO according to the modified Brodie method [3] with different oxidation degrees. Different oxidation degrees were achieved by varying the amounts of KClO₃: 0.5, 1.6, 2.5, 6.4, 8, 16, 22, 32, 35 and 57 in gram of KClO₃ per one gram of graphite (g/g). Combination of analytic techniques (XPS, FTIR, Raman) together with DFT calculations were used to get better insight into the functionalities of graphite oxide.

FTIR/ATR spectra were acquired using Bruker Vertex 70 instrument. XPS spectra were recorded using PHOIBOS 150 analyzer (SPECS) and monochromated Al K α X-ray source. For confocal Raman spectra measurements, Renishaw' inVia system was deployed. Elemental composition of the GO samples was determined by XPS. The only detected elements for all studied samples were carbon and oxygen. At the KClO₃ load of ~ 8-10 g/g the oxygen to carbon XPS line intensities ratio (O/C) saturated at ~1/3. Deconvolution of the high resolved C 1s XPS line for all studied GO samples revealed 3 components assigned to C-C, C-O and C=O bonds. ATR/FTIR spectra for all studied Brodie GO samples were characterized by bands whose positions were different from those typical for Hammers GO. The positions and the relative intensities of the bands of the GO-Brodie samples did not change upon variation of KClO₃ load. In the same time intensities of all the bands in the FTIR spectra showed saturation at the same oxidizer's load of ~ 8-10 g/g as did the O/C XPS signals intensities ratio. To corroborate experimental findings we performed a series of density-functional theory (DFT) studies to provide a molecular-level understanding of the most stable functional groups on a graphene sheet at low coverage. Our DFT results suggest that semiquinoid, carbonyl, carboxyl, ether, and alcohol groups are the most favorable species on graphene when taking into account the adsorption on both sides of the sheet. Comparison of the of the computed vibrational frequencies associated to all these functional groups with experimental FTIR spectra were used to select all possible structures as shown in Fig.1.

References

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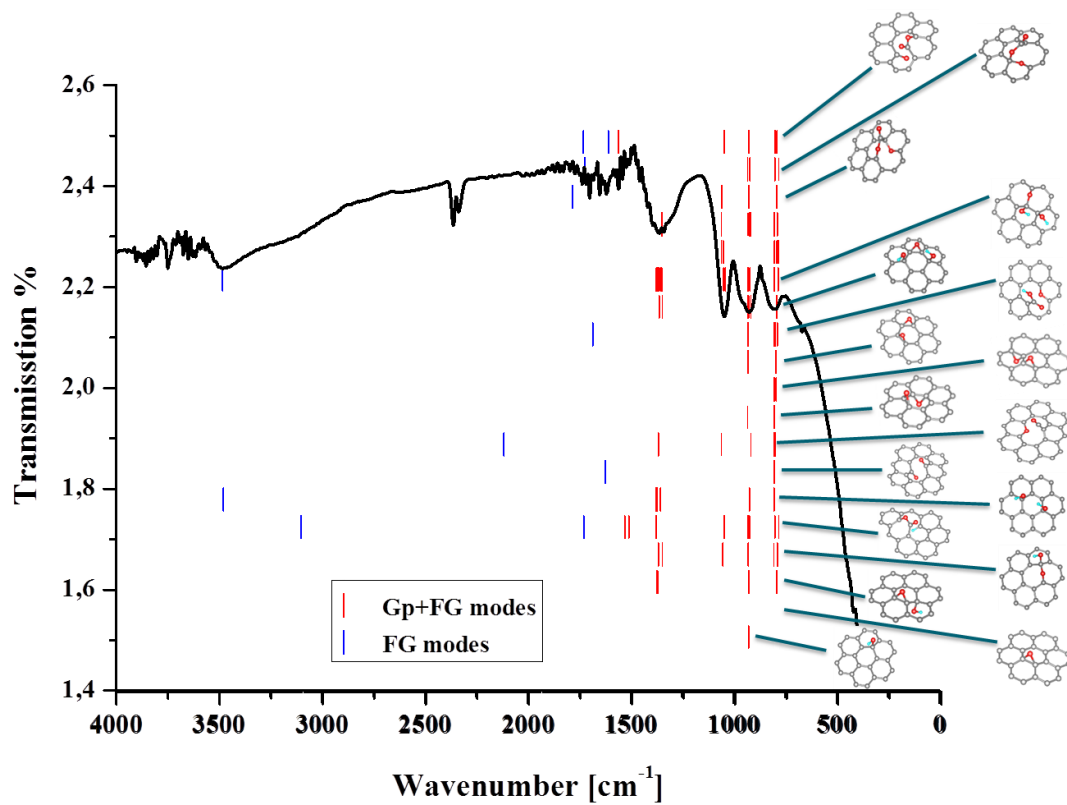


Figure 1. DFT vs FTIR: selection of possible functional groups in Brodie-GO. Gp – vibration modes of graphene layer, FG – vibration modes of functional groups.