Identification of Functional Groups in Brodie Graphite Oxide at Different Degrees of Oxidation

O. Papaianina[1], M. Savoskin[1], A. Vdovichenko[1], **R. Mysyk[1,2],** M. Rodygin[1], I. Nosyrev[1], O. Abakumov[1], O. Bondarchuk[2], T. Rojo[2]

[1]Litvinenko Institute of Physical Organic and Coal Chemistry, NAS of Ukraine, R.Luxemburg 70, 83114, Donetsk, Ukraine
[2]CIC ENERGIGUNE, Parque Tecnológico de Álava, Albert Einstein 48, ED.CIC, 01510 Miñano, Spain

rmysyk@cicenergigune.com

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 ^{0}C, which cannot be explained if only those functional groups are considered [2].

To provide better insight into the functionality of graphite oxide, we synthesized GO of different oxidation degrees by varying the amounts of $KClO_3$ according to the modified Brodie method [3].
The total amount of hydroperoxy and peroxy groups was evaluated on the basis of the iodine released by graphite oxide during 24 h from the solution of potassium iodide and diluted sulfuric acid at 60 ^{0}C. The amount of hydroperoxy groups was determined similarly but using NaI/propan-2-ol, and water was measured using a Karl Fischer titration. ^{13}C solid-state NMR experiments were conducted using a Bruker Avance II 400 instrument (^{13}C 100 MHz, ^{1}H 400 MHz). The samples were packed in 4 mm ZrO_2 rotors and rotated at a MAS rate of 5-12 kHz. ^{13}C cross-polarization magic-angle spinning NMR and the direct pulse method were employed.
FTIR/ATR spectra were acquired using Bruker Vertex 70 instrument. Survey and deconvoluted high resolution C1s and O1s XPS spectra were recorded using PHOIBOS 150 analyzer (SPECS) and monochromated Al Kα X-ray source.

The combined data analysis of ^{13}C solid-state NMR spectroscopy, FTIR, XPS and specific chemical tests has led us to the conclusion that a major fraction of oxygen in Brodie GO is contained in hydroxyl, hydroperoxy and peroxy groups. The quantitative analysis of GO at different degrees of oxidation allowed us to propose two stages in the formation of GO, the first being the hydroxylation of graphene layers with 4-6 hydroxyl groups per coronene fragment (C_{24}) while the second is the build-up of hydroxyl, hydroperoxy and peroxy groups simultaneously involving a significant aromaticity loss in graphene layers. A remarkable result is that the presence of epoxy groups was not evidenced in Brodie GO whereas they are believed to be an abundant part of oxygen-containing groups in widely accepted GO model structures. Finally, a model for Brodie GO (see Figure 1) is suggested on the basis of the collective analysis of all the physical and chemical data.

References

[1] Novoselov K.S., Geim A.K., Morozov S.V. et al., Science, **306** (2004) 666.
[2] Rodríguez A.M., Jiménez P.S.V., **Carbon**, **24** (1986) 163.
[3] Brodie B.C., Phil. Trans. R. Soc. Lond., **149** (1859) 249.

Figures

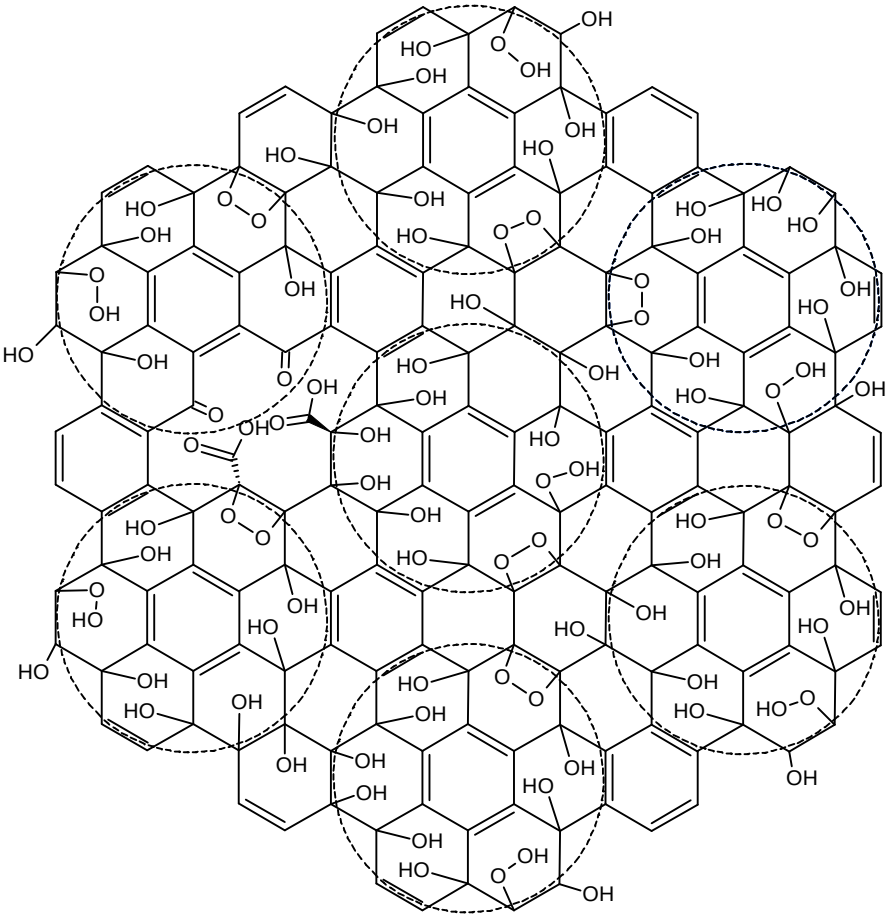

Figure 1. The suggested structure of a single-layer fragment in Brodie graphite oxide