

# **Increasing the efficiency and cycle life of Na-O<sub>2</sub> batteries based on graphene cathodes with heteroatom doping**

M. Enterría <sup>a</sup>, R. Mysyk <sup>a</sup>, L. Medinilla <sup>a</sup>, S. Villar-Rodil <sup>b</sup>, J.I. Paredes <sup>b</sup>, I. Rincón <sup>c</sup>, F.J. Fernández-Carretero <sup>c</sup>, K. Gómez <sup>a</sup>, J.M. López del Amo <sup>a</sup>, N. Ortiz-Vitoriano <sup>a,c\*</sup>

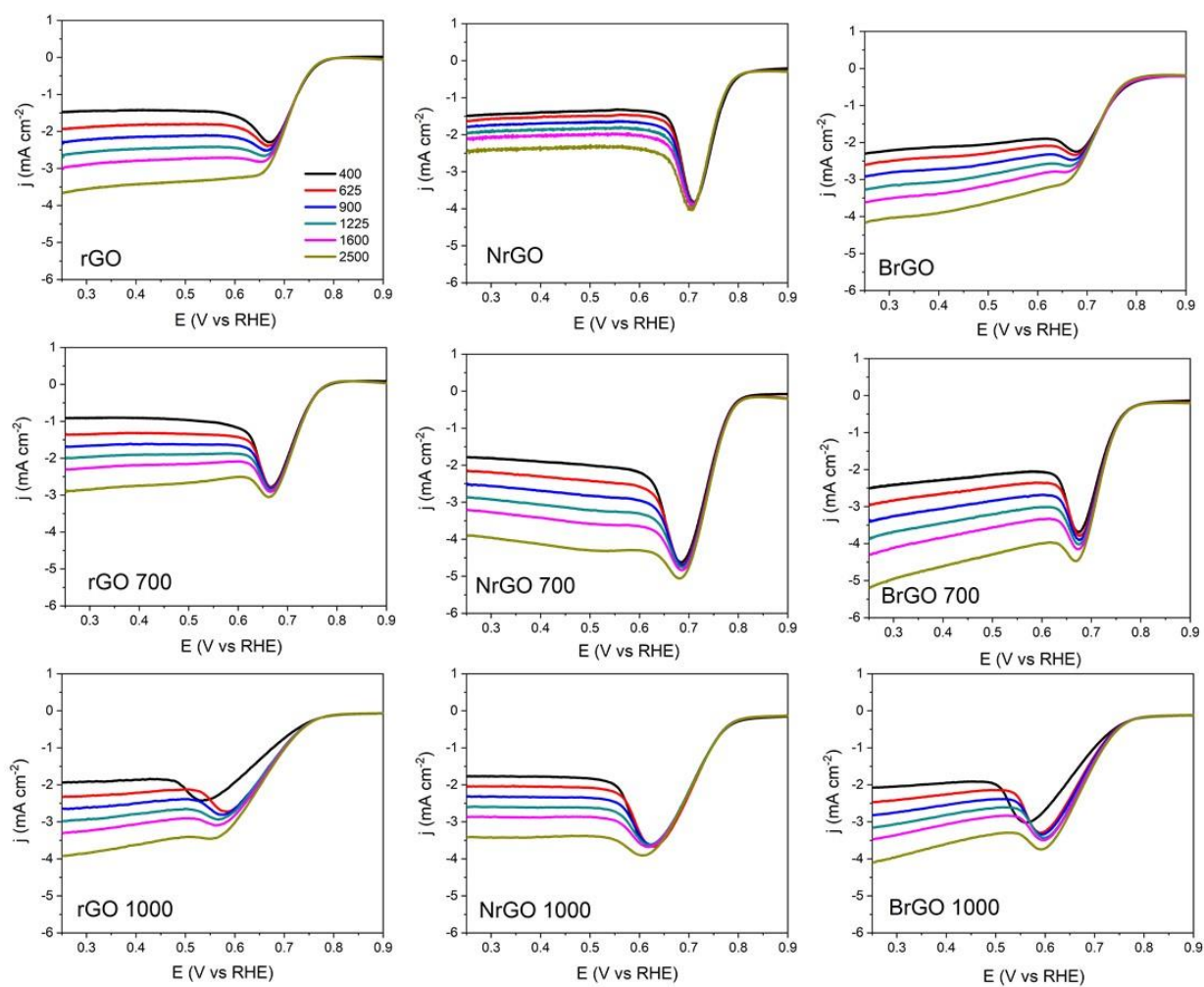
<sup>a</sup> *Center for Cooperative Research on Alternative Energies (CIC energiGUNE), Basque Research and Technology Alliance (BRTA), Alava Technology Park, Albert Einstein 48, 01510.*

<sup>b</sup> *Instituto de Ciencia y Tecnología del Carbono INCAR-CSIC. C/Francisco Pintado Fe 26, Oviedo 33011, Spain*

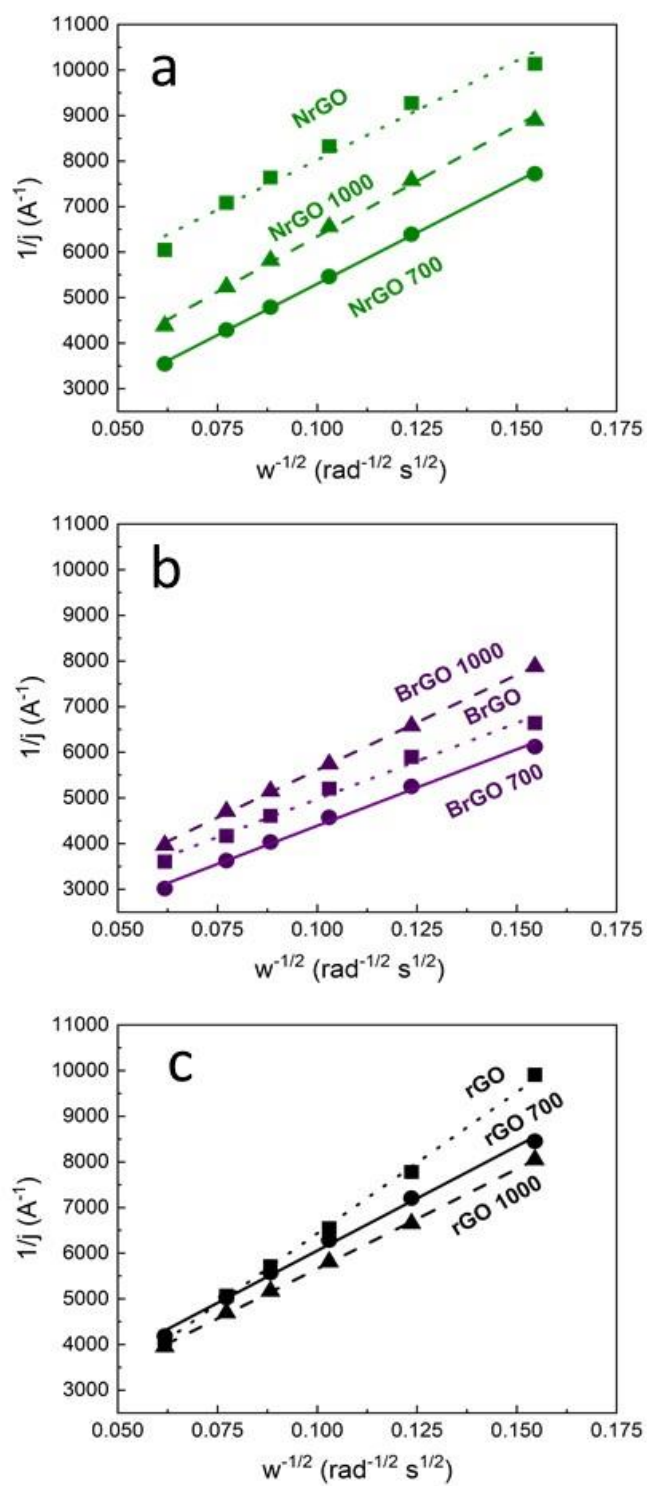
<sup>c</sup> *TECNALIA, Basque Research and Technology Alliance, Mikeletegi Pasealekua, 2, San Sebastián, Spain*

<sup>d</sup> *Ikerbasque, Basque Foundation for Science, María Díaz de Haro 3, 48013 Bilbao, Spain.*

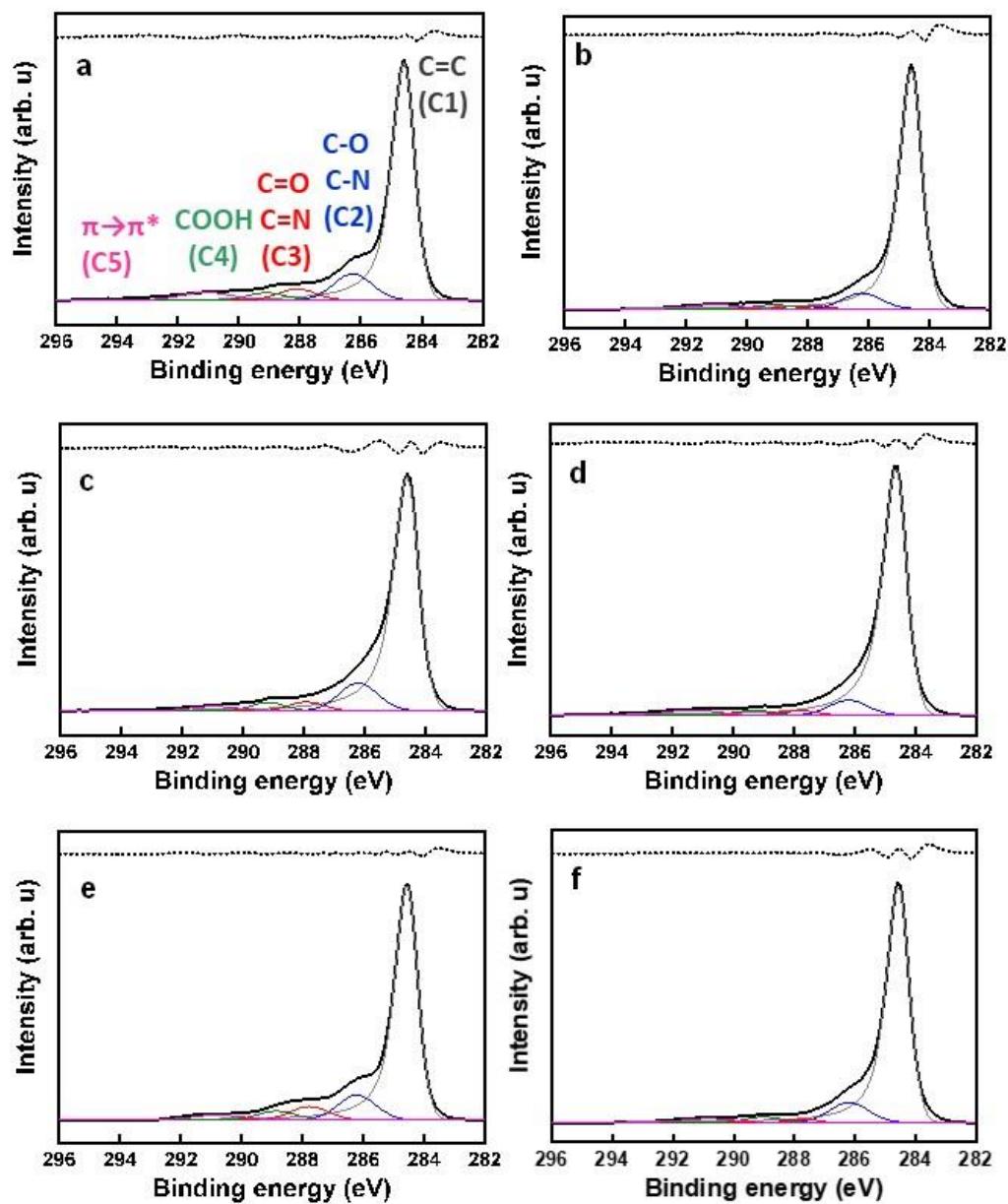
*\*nortiz@cicenergigune.com*



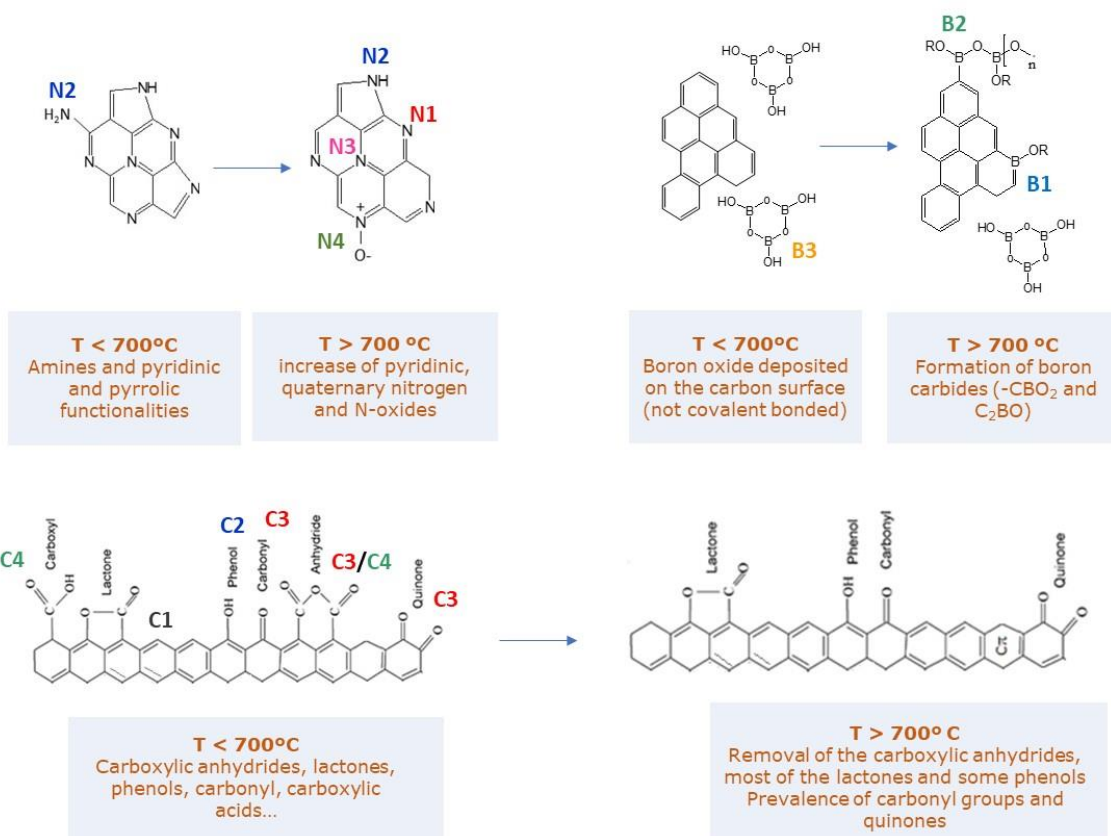
**Figure S1.** LSV curves for all the studied graphene aerogels at different rotation speeds.



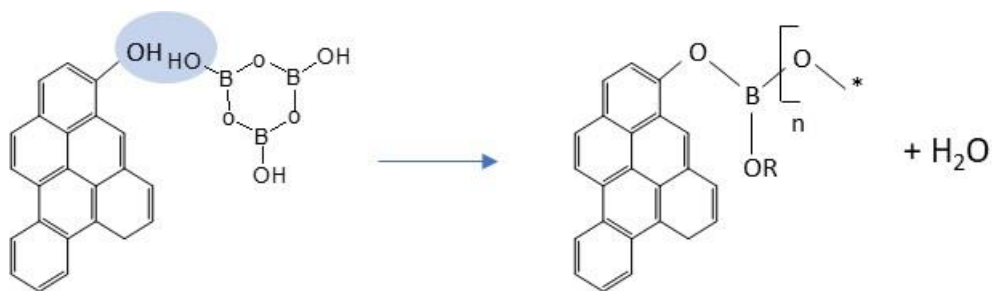
**Figure S2.** Koutecky-Levich study at different rotation speeds for a) rGO, b) NrGO and c) BrGO samples treated at different temperatures.



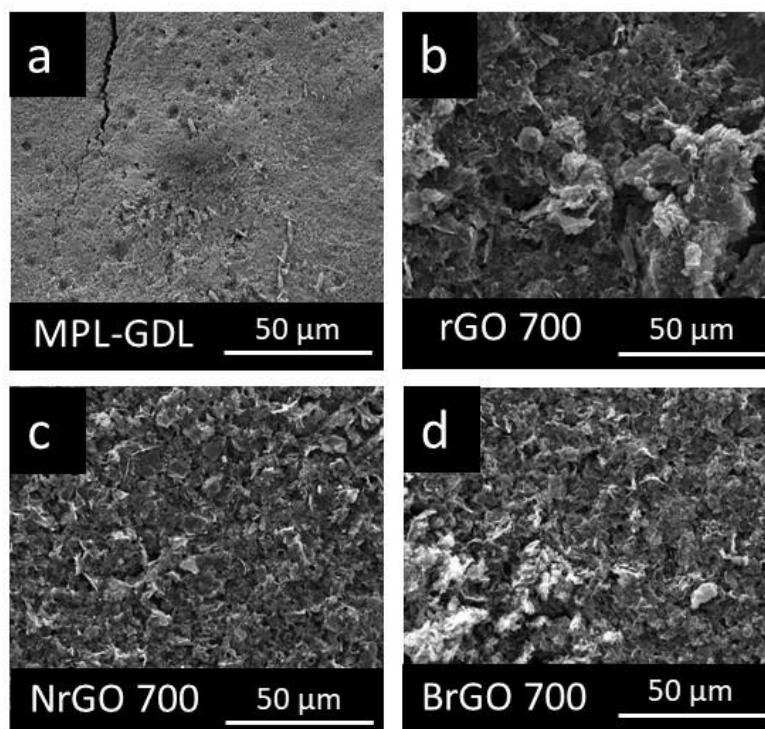
**Figure S3.** C 1s high-resolution core level XPS spectrum of a) rGO, b) rGO 700 °C, c) rGO-N, d) rGO-N 700 °C, e) rGO-B, and f) rGO-B 700 °C. The difference between the experimental and the fitted spectrum (that is, the envelope obtained by addition of the fitted components) is graphed on top of the fitted spectra (black dots).



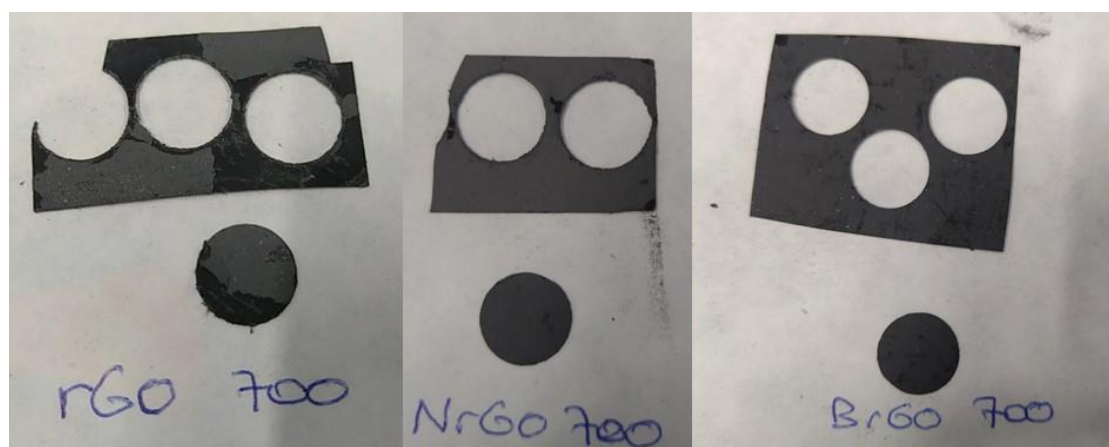
**Figure S4.** Evolution of the chemical state of the different nitrogen, boron and oxygen functionalities with the treatment at 700 °C. Adapted from references [23] and [25] in the main text with the permission of Elsevier.



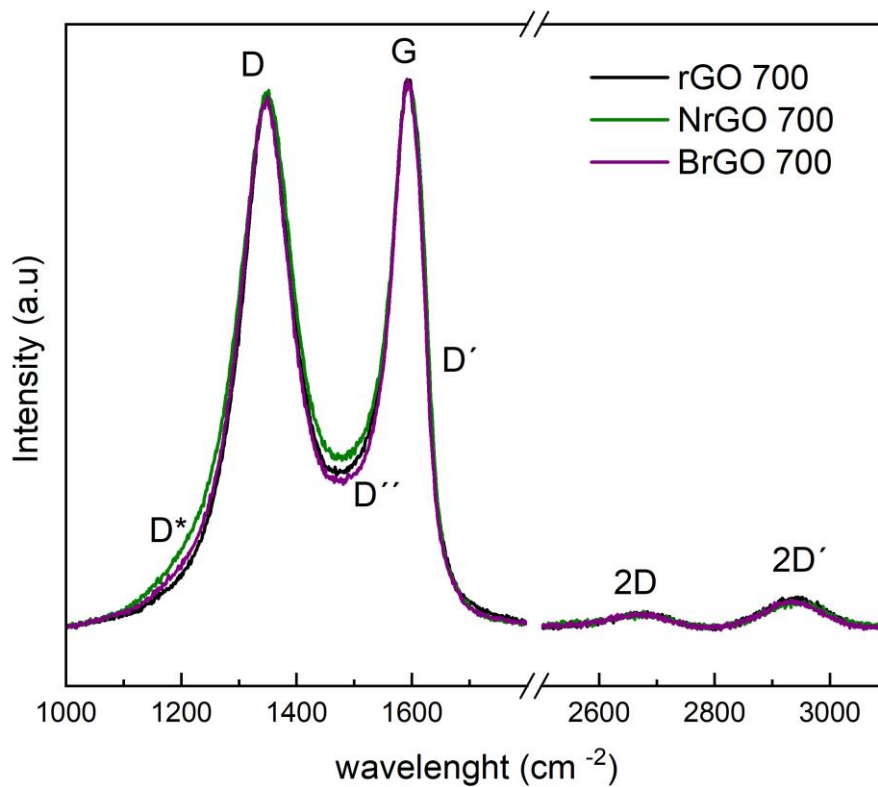
**Figure S5.** Heat treatment-induced condensation of phenol-like functionalities and boron oxides.



**Figure S6.**  $\times 2000$  SEM images of a) the commercial GDL used as support from the microporous layer side and the different GDLs coated with graphene aerogels b) rGO 700, c) NrGO 700, and d) BrGO 700.



**Figure S7.** Images for the aerogel coated-GDLs and the cathodes punched out to be used on the assembled Na-O<sub>2</sub> batteries. The coating in rGO 700 detaches quite easily, in contrast to the good adhesion observed in NrGO 700 and BrGO 700.



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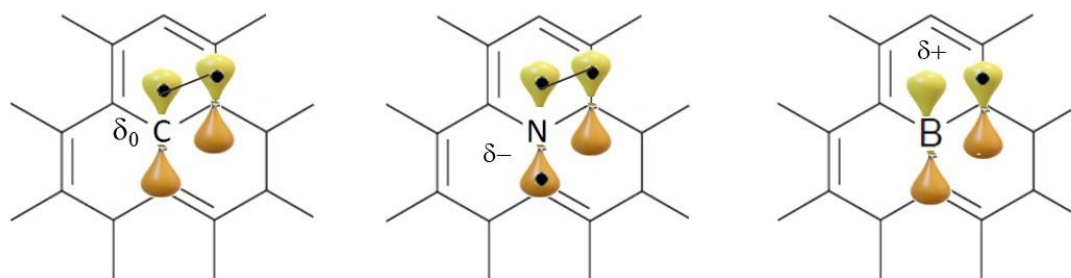
(Relates the intensity of D and G bands with graphite crystallite size)

$$L_a(nm) = \frac{(2.4 \times 10^{-10}) \lambda_l^4}{\frac{I_D}{I_G}}$$

where  $L_a$  stands for graphite crystallite lateral size,  $\lambda_l$  wavelength of the excitation laser,  $I_D$  intensity of the D band (related with disordered domains) and  $I_G$  intensity of the G band (related to ordered domains)

**Figure S8.** Raman spectra for the dry graphene inks after sonication.





**Carbon, 4 electrons in the valence band**

- 3  $\sigma$  bonds with other 3 carbon atoms
- 1  $\pi$ -bond with 1 carbon atom
- No additional free electrons ( $\delta_0$ ) in the  $\pi$ -electron cloud.

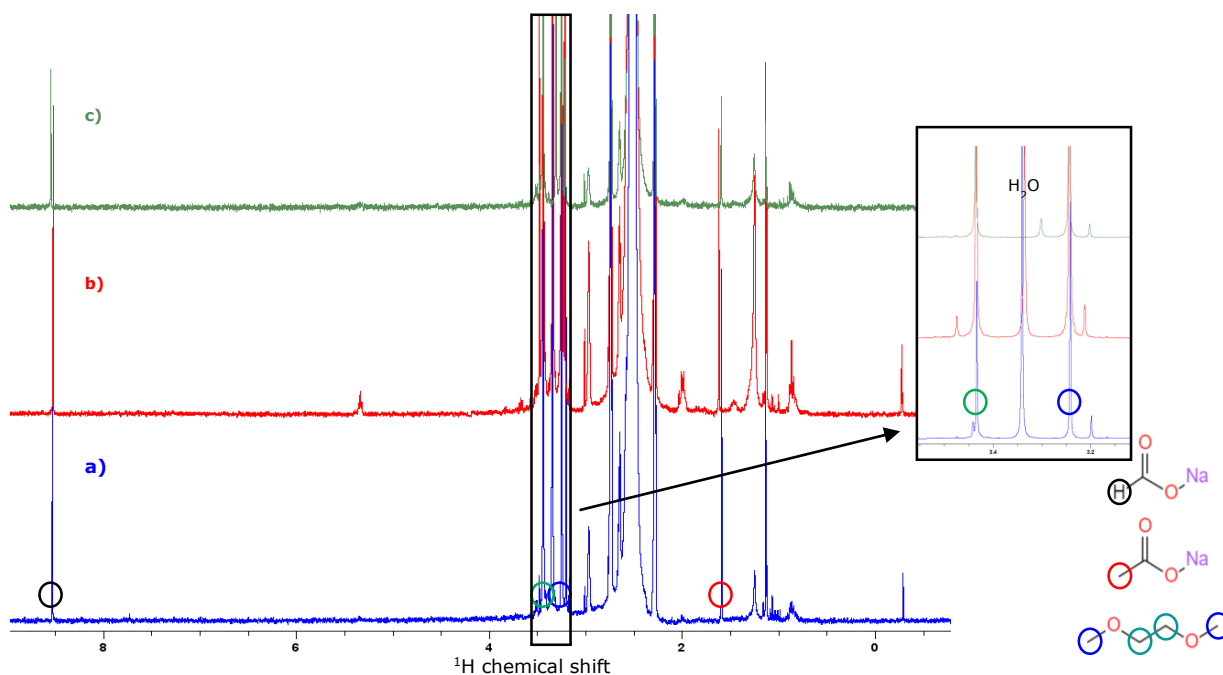
**Nitrogen, 5 electrons in the valence band**

- 3  $\sigma$ -bonds with other 3 carbon atoms
- 1  $\pi$ -bond with 1 carbon atom
- Provides an extra free electron ( $\delta^-$ ) to the  $\pi$ -electron cloud.

**Boron, 3 electrons in the valence band**

- 3  $\sigma$ -bonds with other 3 carbon atoms
- Unable to form an additional  $\pi$ -bond with other carbon atom
- The adjacent carbon gets unsaturated with one unpaired electron, generating a hole in the  $\pi$ -electron cloud ( $\delta^+$ ).

**Figure S9.** Effect of doping on the electronic density of the carbon lattice as function of the introduced heteroatom.



**Figure S10.** Liquid  $^1\text{H}$  NMR spectra of the different extracts after soaking a) rGO 700, b) NrGO 700 and c) BrGO 700 in DMSO for 15h.