

Electronic Supplementary Material

Towards full repair of defects in reduced graphene oxide films by two-step graphitization

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Analysis of high resolution XPS C1s and O1s peaks of the films

Figure S-1 shows high resolution C1s (a) and O1s (b) XPS bands of the reduced graphene oxide (HG) film and their deconvolution. The XPS bands were deconvoluted into Gaussian–Lorentzian components (80:20) after Shirley background subtraction using CasaXPS software.

Figure S-1 (a) High resolution XPS C1s core level spectrum for HG film (black line) and its deconvolution into six components centered at 284.4 eV (navy blue), 285.3 eV (orange), 286.3 eV (cyan), 287.7 eV (pink), 289.0 eV (green), and 290.8 eV (purple). (b) High resolution XPS O1s core level spectrum and its deconvolution into three components centered at 530.5 eV (red), 531.8 eV (cyan), and 533.3 eV (green).

The C1s band was fitted to six components [1-4] **should be [1-4]**, located at binding energies (BE) of 284.6 eV (graphitic C=C species), 285.3 eV (assignment discussed below), 286.3 eV (assignment discussed below), 287.7 eV (C=O), 289.0 eV (COOH), and 290.8 eV ($\pi \rightarrow \pi^*$ shake-up satellite band of graphitic carbon band). The assignment of the 2nd and 3rd component is controversial: While some authors assign them to C–OH and epoxy/ether (C–O) groups [2, 3], respectively, others assign them to defective graphitic structure and C sp³ (free radical, C–O or C–N) [5]. However, whichever deconvolution scheme is considered, this result clearly confirms the success of the reduction process. Indeed, the relative contribution of the

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components associated with oxygenated species is significantly lower than in graphene oxide films [6]. Specifically, while the most prominent component in the unreduced film was the one corresponding to C–O species [4, 6], the graphitic C=C species are dominant after reduction.

Despite some confusion in the literature [7], the generally accepted deconvolution scheme for O1s core level consists of a component at the lowest BE corresponding to doubly-bonded oxygen species (either in

carbonyl C=O or in carboxyl groups O=C-OH) and another component at higher BE corresponding to singly-bonded oxygen (C-O) [8]. Based on XPS analyses of O1s core levels of polymers with known chemical formula [9, 10], singly bonded oxygen is sometimes accounted for with two different components, which, in order of increasing BE, are assigned to oxygen in (C-OH, C-O-C) and to singly-bonded oxygen (O=C-OH, O=C-OR). Sometimes a fourth component assigned to peroxyacid, peroxyester and/or charge effect is considered at the highest BE side. The shape of the experimental O1s band obtained for HG film (Fig. S-1(b)) suggests a deconvolution into three components at 530.5, 531.8, and 533.3 eV corresponding to doubly-bonded oxygen, singly-bonded oxygen in alcohols, ethers and epoxies, and singly bonded oxygen in carboxyls and esters. In previous reports, singly-bonded oxygen in hydroxyls and epoxies has been found to be the dominant moiety [11], which is in agreement with the accepted models for graphite oxide and graphene oxide [12-14]. **Should be [12-14].** Although much less abundant than in its unreduced counterpart, this moiety is again found to be the most prominent in reduced graphene oxide (HG film). As previously reported [11], the intensity of the bands related to groups at the edges of the graphene sheets remains basically unaltered by the reduction process, This agrees with theoretical calculations on the reduction mechanism of GO, which predict a higher difficulty in the removal of oxygen-containing groups located at edges compared to those located at the interior of the basal planes [15].

As shown in Fig. 2 of the original manuscript, the O content falls below the limit of detection of XPS even at the lowest annealing temperature of 1500 °C, so that the C1s band cannot be deconvoluted into different oxygen-containing species. However, after the total elimination of oxygen, the shape of the C1s band is still influenced by the degree of structure restoration attained through healing of defects. Figure S-2 shows normalized high resolution C1s XPS spectra for HG, HG1500, and HG1500-2700 films together with that of HOPG, as reference material.

Figure S-2 Normalized high resolution C1s XPS spectra for HG (red plot), HG1500 (green), HG1500-2700 (orange) films, and HOPG (black). Inset: magnification (~x 40) of the 293–288 eV range.

The increase in intensity of the $\pi \rightarrow \pi^*$ shake-up satellite band of graphitic carbon band (see inset to Fig. S-2) observed between the starting reduced graphene oxide and any of the annealed films is noteworthy. Such an increase reflects the restoration of aromaticity in the material after removal of oxygen atoms. The full width at half maximum (FWHM) of the C1s core level band is sensitive to the heterogeneity of both the chemical and the structural environment of the carbon atoms in the material. Indeed, the first stage of the process, when the chemical environment of the C atoms becomes more homogeneous through the elimination of O atoms, the FWHM falls from 0.86 eV (HG film) to 0.69 eV (HG1500); in the second stage of the structure restoration, when defects such as vacancies are healed, the FWHM diminishes further, specifically, to 0.63 eV (HG1500-2700), which approaches to the value of 0.60 eV displayed by HOPG.

Raman analyses of films prepared with a one-stage treatment

Reduced graphene oxide paper samples were subjected to high temperature annealing (2100 and 2400 °C) in a graphite furnace under argon flow (2 L min⁻¹). The heating rates were the same as indicated in the manuscript (see Experimental section). Once it was reached, the target temperature was kept constant for 1 h

and finally the samples were cooled down to room temperature while maintaining the same argon flow. The graphitized samples are designed HG2100 and HG2400. Figure S-3 shows their normalized Raman spectra.

Figure S-3 Normalized Raman spectra for HG2100 (brown) and HG2400 (blue).

The corresponding I_D/I_G values are 0.06 (HG2100) and 0.04 (HG2400), which, taking into account that the error is estimated to be ± 0.01 -0.03, are similar to those obtained for the samples annealed at the same maxima temperatures but with a two-step process with intermediate annealing at 1500 °C, namely 0.09 (HG1500-2100) and 0.07 (HG1500-2400) (see Fig. 3(b) and Table 1 of the manuscript).

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