

# Thermally Stable, Solvent Resistant and Flexible Graphene Oxide Paper

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## Supplementary Material

### *Wide angle X-ray diffraction methods*

Wide-angle X-ray diffraction (WAXD) patterns were obtained by an automatic Bruker D8 Advance diffractometer, in reflection, at 35 KV and 40 mA, using the nickel filtered Cu-K $\alpha$  radiation (0.15418 nm). The *d*-spacings were calculated using Bragg's law and the observed integral breadths ( $\beta_{\text{obs}}$ ) were determined by a fit with a Lorentzian function of the intensity corrected diffraction patterns, according to the procedure described by Iwashita et al.<sup>1</sup> The instrumental broadening ( $\beta_{\text{inst}}$ ) was also determined by fitting of Lorentzian function to line profiles of a standard silicon powder 325 mesh (99%). For observed reflections, the corrected integral breadths were determined by subtracting the instrumental broadening of the closest silicon reflection from the observed integral breadths,  $\beta = \beta_{\text{obs}} - \beta_{\text{inst}}$ . The correlation lengths (*D*) were determined using Scherrer's equation.

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where  $\lambda$  is the wavelength of the incident X-rays and  $\theta$  the diffraction angle, assuming the Scherrer constant  $K = 1$ .

Wide-angle X-ray diffraction measurements were also obtained by using a cylindrical camera (radius = 57.3 mm). The WAXD patterns of papers were recorded on a BAS-MS imaging plate (FUJIFILM) and processed with a digital imaging reader (FUJIBAS 1800). In particular, to characterize the orientation of the graphene planes, photographic X-ray diffraction patterns were

taken by placing the papers parallel to the axis of the cylindrical camera and by sending the X-ray beam parallel or perpendicular to the paper surface (EDGE and THROUGH measurements, respectively, see scheme in the lower part of Figure 1).

The degree of parallelism of the graphitic planes with respect to the paper plane has been formalized on a quantitative numerical basis using Hermans' orientation functions, in analogy to that one defined for the uniplanar orientation of polymers<sup>2,3</sup>:

$$f = (\overline{\cos^2 x} - 1)/2 \quad (2)$$

by assuming  $\overline{\cos^2 x}$  as the squared average cosine value of the angle,  $x$ , between the normal to the film surface and the normal to the graphitic planes.

The quantity  $\overline{\cos^2 x}$  has been experimentally evaluated, by using the following equation:

$$\overline{\cos^2 x} = \overline{\cos^2 \chi} = \frac{\int_0^{\pi/2} I(\chi) \cos^2 \chi \sin \chi d\chi}{\int_0^{\pi/2} I(\chi) \sin \chi d\chi} \quad (3)$$

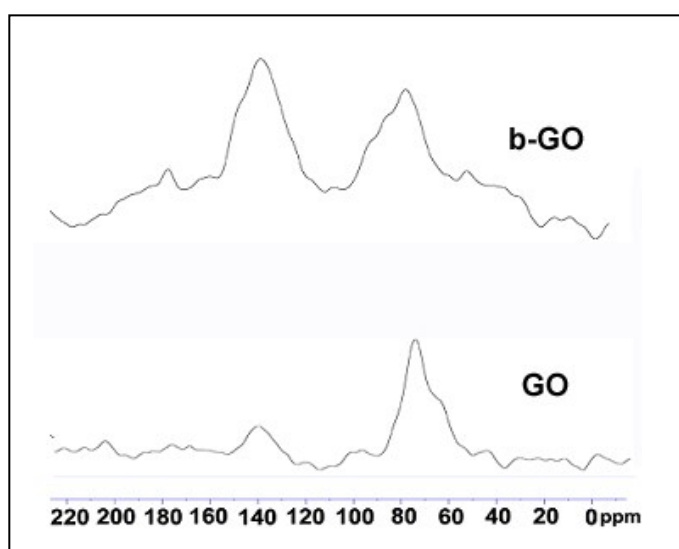
where  $I(\chi)$  is the intensity distribution along rings at constant  $2\theta$  value corresponding to maximum intensities, and  $\chi$  is the azimuthal angle measured from the equator. The diffracted intensities  $I(\chi)$  of eq. 3 were obtained by EDGE patterns, as collected by using a cylindrical camera. Because the collection was performed at constant  $2\theta$  values and in the equatorial geometry, the Lorentz and polarization corrections were unnecessary.

In these assumptions, the orientation factor  $f$  of the graphitic planes is equal to 1 and -0.5 if all GO planes are perfectly parallel and perpendicular to the plane of the paper, respectively.

### *NMR Characterization*

Solid-state  $^{13}\text{C}$  NMR experiments were performed on the Bruker Avance 300 MHz spectrometer operating at 75.48 MHz for  $^{13}\text{C}$ . The samples were packed in the zirconium rotors of 4 mm and

were spun at a rate of 9 kHz, which is fast enough to 30 remove spinning sidebands for aliphatic and aromatic carbons at this field strength. The spectra were acquired using magic-angle spinning with cross polarization pulse sequence (CP-MAS) with a contact time of 5 ms, at room temperature by using a pulse length of 2.9  $\mu\text{s}$  ( $90^\circ$ ) with an acquisition time of 0.022 s and a recycle 35 time of 5 s to ensure quantitative detection. For each spectrum 30 K transients were accumulated. All  $^{13}\text{C}$  peaks were referenced to the upfield peak of adamantane centred at  $\delta = 29.5$  ppm.



**Figure S1.  $^{13}\text{C}$  CP MAS NMR spectra of GO a) before and b) after alkaline treatment**

The significant structural changes associated with GO basification were also studied by solid-state  $^{13}\text{C}$  technique. The spectrum of GO as prepared by Hummers' oxidation shows a substantial presence of C-OH and C-O-C epoxy bonds at 70 and 63 (shoulder), respectively.<sup>4</sup> Deep differences are, instead, present in basified GO paper, with a complete disappearance of the epoxide functionalities at 62.6 ppm. The shift of the band maximum from 70 to 74 ppm, could be compatible with additional formation of C-OH and C-O-C ether bonds.<sup>5,6</sup> For the basified GO, also a strong resonance at 130 ppm, related to the un-oxidized  $\text{sp}^2$  carbon of the graphene network coming from a partially decarboxylation, is observed.

## REFERENCES

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