Supporting Information: A comparative Electron Paramagnetic Resonance study of expanded graphites and graphene

Francesco Tampieri^a, Simone Silvestrini^a, Raffaele Riccò^b, Michele Maggini^a, Antonio Barbon^{a*}

We report here the SEM images of the samples studied, the results of the XRD measurements, together with the results of the EPR and Raman spectroscopies not shown in the main text.

SEM images

Here are reported the SEM images of samples EH, EK, EHK and RGO at different enlargement that evidence the different degrees of exfoliation obtained for different samples. The SEM image of sample RGO has been obtained from the technical datasheet of the sample.



Figure S1 SEM images of sample EH, EK, EHK and RGO. The scale is indicated in each picture. The SEM image for sample RGO comes from the technical data sheet of the sample.

XRD measurements

XRD patterns recorded for the samples EH, EK, EHK and RGO are reported in Figure S2, along with the data from the starting material. In the spectra, the (002), the (100), (101) and (004) reflections are observed at about 26°, 42° 44° and 54° respectively¹. Comparison between different samples can be made by comparing the (002) peaks, which are associated to the interplanar distance

between graphene sheets packed into the graphitic structure and to the dimension of the stacking. Table S1 reports both the angular position and FWHM parameter of the (002) reflections.

The spectra of the samples can be interpreted as superpositions of two types of reflections, one narrow, centered at 26.44° of the starting material (SM), and one broad, typical of RGO. The narrow-line reflection is strong only for EH sample, for which the elastic scattering tail (due to amorphous parts) at low angle values is almost unobservable.

The data in Table S1 show that, for samples EH, EK and EHK, the narrow peaks have a FWHM of $0.45 \div 0.51^{\circ}$, much broader than that of SM. It is possible to have a rough estimate of the number of stacked layers by applying the Scherrer equation²:

$$L_{a,c} = \frac{k_{a,c}\lambda}{FWHM\cos\theta}$$

Where $k_{a,c}$ is a constant (0.9) for the observed reflection, λ is the instrument wavelength of the line centered at the given θ value. Because of the inhomogeneity of the sample, we consider the obtained numbers representative of the average structures. From the above equation we found that the thickness of the stacks (L_c) is about 260 Å, that corresponds to 70-80 stacked graphene layers. Samples EK and EHK, which are dominated by broader signals, 3.3 to 10° wide, have fewer stacked graphene layers: about 14 layers for EK and 23-41 layers for EHK. For these samples the low-angle component is clearly visible, indicating likely the presence of

Information about the lateral L_a dimension can be obtained from the FWHM values of the (100) reflections, that are evident for EK,

EHK and RGO samples. In this case the Scherrer equation enables to obtain the values of $L_a = 0.16, 0.12$ and 0.02 µm respectively.



Figure S2 Powder diffraction patterns for SM, EK, EH, EHK and RGO samples,

Table S1 Position and linewidth (FWHM) of the XRD (002) peaks for the relative samples in fig. S2.

Sample	Peak 1 (002)					
	Pos (°)	FWHM (°)	Ampl			
RGO	23.9	7.9	810			
KOO	29.5*	10.1	500			
	26	0.57	6100			
FIL	26.36	0.51	6600			
EП	26.66	0.3	3200			
	27.83*	1.2	1800			
FIZ	24.6	10	164			
EK	26.4	0.48	100			
ЕНК	22	6	350			
	26.02	3.3	417			
	26.44	0.47	314			
	30*	10	400			
SM	26.44	0.13	180			

* likely (002) reflection of graphite in rhombohedral form (J.-T. Wang, C. Chen, E. Wang, Y. Kawazoe Sci. Rep. 4 (2013) 4339).

Raman

The Raman spectra of the studied samples at room temperature, normalized for the G band intensity, are displayed in Figure S3.

Since in most cases the bands appeared to be multicomponent, we deconvoluted them as sum of Lorentzian lines. For the D, G and D' bands we used one Lorentzian component, while for the 2D band up to four components were used in order to obtain the best reproduction in agreement also with studies in literature³⁻⁶. The parameters obtained from the deconvolution of the Raman spectra of all samples are collected in Table S2.

The D' band is evident in the spectrum of sample EH at 1606 cm⁻¹, it can be observed in samples EK and EHK as a shoulder of the G band and it is apparently absent in sample RGO or hidden under the much wider G band.

The 2D bands for samples EH, EK and EHK are given by the sum of three or four components, their positions and intensities, compared to those of the relative G bands, are similar for the three samples and are similar also to what has already been reported in the literature for polycrystalline graphites⁷.

The 2D band of the sample RGO, observed after subtraction of a 2000-3000 cm⁻¹ broad component⁸, instead is much wider than the other samples. This band was deconvoluted using three Lorentzian components.

Sample	Band	Raman shift [cm-1]	Width [cm ⁻¹]	Amplitude /10 ⁴ [a. u.]
RGO	D	1337.13 ± 0.31	147.7 ± 1.3	580.3 ± 5.3
	G	1489.04 ± 0.23	83.26 ± 0.84	325.8 ± 3.1
	$2D_1$	2396±5	350	50
	$2D_2$	2665±1	390	250
	2D ₃	2925±1	210	100
EH	D	1336.96 ± 0.33	51.4 ± 1.1	4.265 ± 0.081
	G	1582.577 ± 0.027	14.374 ± 0.090	8.623 ± 0.048
	D'	1605.94 ± 0.15	17.55 ± 0.51	2.129 ± 0.054
	$2D_1$	2651.7 ± 1.3	69.2 ± 2.7	6.32 ± 0.41
	$2D_2$	2687.73 ± 0.25	31.9 ± 1.4	4.96 ± 0.32
	2D ₃	2715.80 ± 0.91	17.0 ± 3.3	0.393 ± 0.089
EK	D	1321.28 ± 0.23	71.98 ± 0.86	29.92 ± 0.33
	G	1578.443 ± 0.097	27.71 ± 0.32	20.75 ± 0.21
	D'	1607.76 ± 0.51	14.1 ± 1.7	1.29 ± 0.14
	$2D_1$	2605 ± 14	104 ± 15	4.0 ± 2.0
	$2D_2$	2643.9 ± 2.1	51 ± 12	5.4 ± 2.6
	2D ₃	2673.1 ± 1.3	32.2 ± 8.8	3.3 ± 1.8
	$2D_4$	2692.7 ± 2.2	27.8 ± 5.0	1.65 ± 0.79
EHK	D	1318.21 ± 0.28	82.4 ± 1.1	35.80 ± 0.44
	G	1576.04 ± 0.11	32.62 ± 0.38	25.21 ± 0.25
	D'	1605. 3 ± 1.2	7.3 ± 4.1	0.21 ± 0.10
	$2D_1$	2603 ± 11	114 ± 13	5.1 ± 1.8
	$2D_2$	2645.4 ± 2.2	49.9 ± 8.9	6.2 ± 2.4
	2D ₃	2671.6 ± 1.2	32.1 ± 9.0	3.2 ± 1.7
	$2D_4$	2691.7 ± 1.9	26.2 ± 4.9	1.42 ± 0.65
SM	D	1335.41 ± 0.55	42.0 ± 1.8	3.68 ± 0.12
	G	1582.812 ± 0.027	16.359 ± 0.083	18.015 ± 0.069
	D'	1662.12 ± 0.55	6.9 ± 1.6	0.241 ± 0.042
	$2D_1$	2646.3 ± 1.5	60.0 ± 4.1	8.73 ± 0.76
	$2D_2$	2689.34 ± 0.39	38.3 ± 1.3	12.98 ± 0.58

Table S2 Parameters derived from the fit of the bands D, G, D' and 2D for all samples. No D' band was observed for sample RGO, the 2D band was fitted using two to four components.



Fig. S3 Raman spectra of samples SM, RGO, EH, EK and EHK at 622 nm.

Electron Paramagnetic Resonance results

Here are reported the cw-EPR spectra for all samples at room temperature and at some selected temperatures together with the simulations. The parameters obtained from the simulations at the same temperatures are collected in the tables. The trend of the EPR intensities and the principal values of the **g**-tensors with the temperature are also reported for all the samples.

Sample EH



Figure S3 cw-EPR of EH sample at selected temperatures (black) with their simulations (red, two Dysonian components). The profile shows a decrease of the intensity lowering the temperature. The S/N ratio obtainable with this sample is very low.

Table S3 Relevant simulation parameters of the cw-EPR spectra at selected temperature for sample EH. For each contribution i, the linewidth, the g-value, the asymmetry parameter α for the Dysonian lineshape and the relative abundance of the species (C_i) is indicated.

T [K]	%C ₁	\mathbf{g}_1	Γ ₁ [G]	\mathbf{g}_2	Γ_2 [G]	a2
295	82	2.0036	17.30 ª	2.0027	6.57 ^b	1.8
205	94	2.0060	16.00 ^a	2.0035	7.10 ^b	6.2
150	97	2.0054	18.60 ^a	2.0036	5.49 ^b	2.9

^a bulk graphite lineshape ⁹

^b general Dysonian lineshape ¹⁰



Figure S4 Intensity variation for each of the two components of the cw-EPR spectrum for sample EH as function of the temperature (red points = EH-1, blue points = EH-2).



Figure S5 g-principal values variation for each of the two components of the cw-EPR spectrum for sample EH as function of the temperature (red points = EH-1, blue points = EH-2).

Sample EK



Figure S6 cw-EPR of EK sample at selected temperatures (black) with their simulations (red, two Lorentzian components). The profile shows the narrowing of the band at the lowest temperature and an increase of the intensity.

Table S4 Relevant simulation parameters of the cw-EPR spectra at selected temperature for sample EK. For each contribution i, the linewidth, the perpendicular (subscript label a) and parallel (subscript label b) components of the g-tensors are reported. The relative abundance of the species (C_i) is indicated.

T [K]	% C ₁	g ₁	Γ ₁ [G]	g _{2a}	g_{2b}	$\Gamma_2[G]$
290	1.6	2.0016	3.37 ª	2.0027	2.0027	10.9 ^a
150	4.0	2.0027	4.53 ^a	2.0029	2.0051	11.4 ^a
16	15	2.0031	4.56 ª	2.0022	2.0065	9.8 ^a

^a Lorentzian lineshape

The variation with the temperature of the two components of sample EK is reported in the main text.



Figure S7 g-principal values variation for each of the two components of the cw-EPR spectrum for sample EK as function of the temperature (red points = EK-1, blue points = EK-2).

Sample EHK



Figure S8 cw-EPR of EHK sample at selected temperatures (black) with their simulations (red, two Lorentzian components). The profile shows an increase of the intensity at the lowest temperatures. The spectrua at 140 K and 7.5 K are multiplied by a factor 2.

Table S5 relevant simulation parameters of the cw-EPR spectra at selected temperature for sample EHK. For each contribution i, the linewidth, the perpendicular (subscript label a) and parallel (subscript label b) components of the g-tensors are reported. The relative abundance of the species (C_i) is indicated.

T [K]	%C ₁	\mathbf{g}_{1a}	$\mathbf{g}_{1\mathbf{b}}$	Γ ₁ [G]	\mathbf{g}_{2a}	$\mathbf{g}_{2\mathbf{b}}$	Γ ₂ [G]
290	27.5	2.0022	2.0065	5.23 ª	2.0026	2.0093	10.70 ^a
140	21.4	2.0027	2.0078	4.90 a	2.0035	2.0109	12.90 ª
7.5	21.3	2.0026	2.0047	3.31 a	2.0041	2.0041	9.61 ^a

^a Lorentzian lineshape



Figure S9 Intensity variation for each of the two components of the cw-EPR spectrum for sample EHK as function of the temperature (red points = EHK-2). The intensity of both components increase with temperature at higher temperatures, typical behaviour of zero-gap semiconductors. The inset shows an enlargement of the graph at higher temperatures.



Figure S10 g-principal values variation for each of the two components of the cw-EPR spectrum for sample EHK as function of the temperature (red points = EHK-1, blue points = EHK-2).

Reduced Graphene Oxide (RGO)



Figure S11 cw-EPR of RGO sample at selected temperatures (black) with their simulations (red, two Lorentzian components). The profile shows an increase of the intensity at the lowest temperatures. The spectrum at 150 K is multiplied by a factor 5 and the spectrum at 10 K by a factor 0.01.

Table S6 Relevant simulation parameters of the cw-EPR spectra at selected temperature for sample RGO. For each contribution i, the linewidth, the g-value and the relative abundance of the species (C_i) is indicated.

T [K]	%C ₁	\mathbf{g}_1	Γ ₁ [G]	\mathbf{g}_2	$\Gamma_2[G]$
290	20.3	2.0031	4.41 a	2.0032	12.97 ª
150	6.3	2.0039	11.95 a	2.0039	48.34 ^a
80	22.3	2.0024	2.86 ª	2.0028	16.21 ^a
10	33.6	2.0035	1.45 ^a	2.0037	6.12 ^a

^a Lorentzian lineshape



Figure S12 Intensity variation for each of the two components of the cw-EPR spectrum for sample RGO as function of the temperature (red points = RGO-1, blue points = RGO-2). The intensity of both components increase with temperature at higher temperatures, typical behaviour of zero-gap semiconductors. The inset shows an enlargement of the graph at higher temperatures.



Figure S13 g-principal values variation for each of the two components of the cw-EPR spectrum for sample RGO as function of the temperature (red points = RGO-1, blue points = RGO-2).

References

- 1 G. Parhasarathy, A. S. Collins and T. Chetty, Journal of the Geological Society of India, 2006, 68, 176-180.
- 2 N. Kumar, A. Shukla, J. Singh, M. K. Patra, P. Ghosal and S. R. Vadera, Graphene, 2013, 1, 63-67.
- 3 I. Calizo, S. Ghosh, W. Bao, F. Miao, C. Ning Lau and A. A. Balandin, Solid State Commun., 2009, 149, 1132-1135.
- 4 M. S. Dresselhaus, A. Jorio, M. Hofmann, G. Dresselhaus and R. Saito, Nano Letters, 2010, 10, 751-758.
- 5 A. C. Ferrari, Solid State Commun., 2007, 143, 47-57.
- 6 D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold and L. Wirtz, Nano Letters, 2007, 7, 238-242.
- 7 F. Tuinstra and J. L. Koenig, J. Chem. Phys., 1970, 53, 1126.
- 8 Y. Li, Z. Li and P. K. Shen, Adv Mater, 2013, .
- 9 G. Wagoner, *Physical Review*, 1960, **118**, 647.
- 10 J. P. Joshi and S. Bhat, Journal of Magnetic Resonance, 2004, 168, 284-287.