

Electronic Supplementary Information

Vortexes tune chirality of graphene oxide and its noncovalent hosts

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Experimental detail

GO was synthesized following an improved Hummer procedures [H. W. Hummers and R. E. Offeman. *J. Am. Chem. Soc.* 1958, **80**(6), 1339-1339; D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, A. Sun, A. Slesarev A, L. B. Alemany, W. Lu and J. M. Tour *ACS Nano*, 2010, **4**(8), 4806-4814]. All GO work solutions was prepared dissolving the solid in ultrapure water obtained from Elga Purelab Flex system by Veolia, performing 45 minutes sonication, to obtain concentration ranging from 10mg/L to 50 mg/L.

UV/Vis and Circular Dichroism spectra were acquired at room temperature on a JASCO V-530 spectrophotometer and a JASCO J-810 spectropolarimeter respectively, using a 1 cm quartz cuvette.

Drop casting deposition on quartz under stirring experiments were performed putting a 100 µL drop of GO solution onto clean quartz, placed on the magnetic plates, then we set a small magnetic bar inside the GO drop. After 30 minutes slow stirring (CW or CCW) the drop is completely dried, then we stop the stirrer and remove the magnetic bar and perform the spectroscopic analysis.

In order to avoid artifacts we performed CD spectra at different angular orientation of the quartz substrate. LD measurements were performed by using a home-modified JASCO J500A instrument, equipped with a 150W Xenon lamp. The measurements were carried out at different rotation angle of the polarizer/PE modulator system (necessary set-up for liquid samples), defined as relative to the horizontal orientation [P. Mineo, V. Villari, E. Scamporrino and N.

Micali Soft Matter, 2014, **10**, 44–47]. An analyzer was used for the calibration of LD and for the separate measurement of the birefringence of the optical system. All these measurements allowed for evaluating quantitatively the cross-talk between LD and CD.

AFM analysis was carried out in semi contact mode using a NT-MDT system. Si HA_NC Etalon tips were used (Force constant, 12 N/m, resonance frequency, 235 kHz): working resonance and set point were varied to control the force between the Si tip and the substrate.

Zeiss Supra 55VP Field Emission Scanning Electron Microscope was used for morphological characterization of GO deposited by drop-stirring on silicon wafer.

Circular dichroism of standing solutions:

CD spectra, at concentration of about 20 mg/l — very much similar to that already published [29] — show a positive dichroic envelope, with maxima at the same wavelength of the absorption spectrum (Figure S1). The origin of GO chirality is not a simple issue because it is hard to consider a GO sheet as a “molecule”; as a consequence of the size, it has already the degree of complexity of a “supramolecular system”. We observe that manual shaking of the cuvette induces remarkable variation of the CD intensity. Figure S8 shows that after any manual shaking (red arrow) the CD intensity starts from different values; sometimes it grows and sometimes it decreases. We also observe that the intensity varies even if the cuvette is very gently removed and reinserted into the instrument. In addition, the existence of residual birefringence and alignment effects (linear dichroism) makes the correct evaluation of the optical activity a complicated task. However, it is likely that the large GO sheets might adopt chiral conformations. This issue of the chirality of static samples is currently under study in our laboratory.

At low concentration value (typically 10 mg/l) the colloidal solution is isotropic and a shear flow is not able to induce birefringence, as shown in the first section.

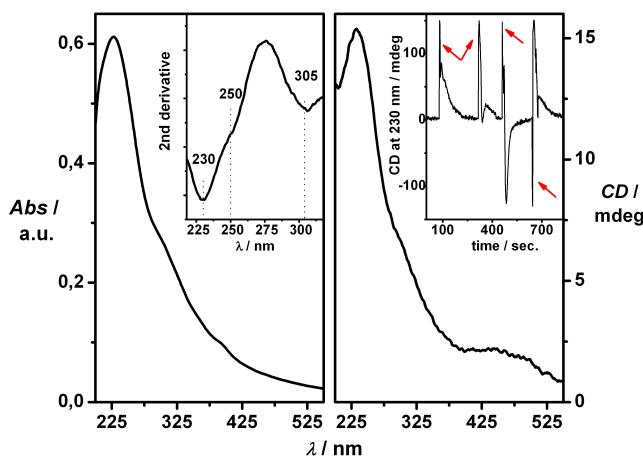


Figure S1. Left: absorption spectrum of GO aqueous solution. The inset shows the 2nd derivative of the spectrum; right: CD spectrum of an aqueous solution of GO. The inset shows the effect of a gentle shaking of the cuvette on the CD intensity *vs* time (red arrows indicate the instant of shaking of the cuvette).

Estimation of LD contribution and birefringence

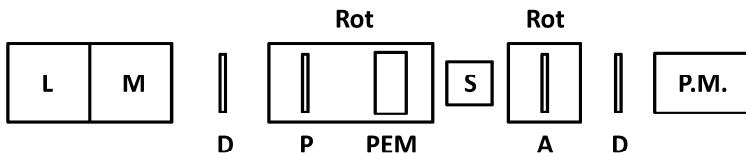
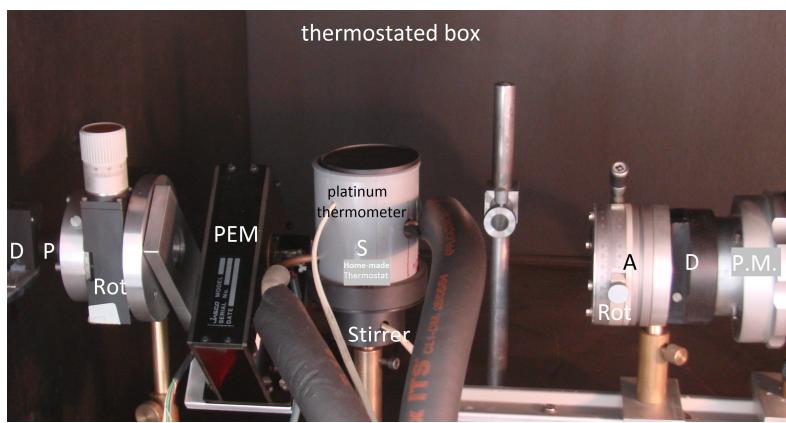
The measured LD and CD spectra are given by:

$$LD_{meas} = G_2 LD_\chi \cos(2(\chi - \theta_P)) \quad (S1a)$$

and

$$CD_{meas} = G_1 [CD + 0.5(LD'LB - LDLB') + \frac{LD_{meas}}{G_2} \sin\alpha] \quad (S1b)$$

where G_2 is known from calibration, θ_P is the orientation of polarizer/PEM (see Scheme S1) and χ represents the orientation of the linear dichroism, both considered with respect to the horizontal direction. Moreover, LB and LD are the linear birefringence and the linear dichroism, respectively, and LD' and LB' the 45° linear dichroism and 45° linear birefringence, respectively.



Scheme S1. Photograph and scheme of the modified spectropolarimeter. L=lamp, M=Monochromator, D=Depolarizer, P=Polarizer, PEM=Photoelastic modulator, ROT= Rotator stage, S=Sample, A=Analyzer, P.M.=Photomultiplier.

The residual static birefringence of PE modulator α of our modulator is negligible (indeed CD_{meas} is independent from θ_P), therefore, LD contributes to the measured CD only through the coupling with LB (cross-talk).

The concentrated GO solution (50 mg/L) shows birefringence, like liquid crystals; indeed, the measured dichroism signal depends on the chosen cuvette side. For lower concentrations (but above 10 mg/L) the solution does not exhibit birefringence even under stirring, but a significant LD is still present both in the standing (figure S2) and in the stirred solution (figures S3 and S4). The measurements performed at different angles, between the polarizer/PE modulator orientation and the horizontal direction, gives the LD amplitude ($LD_\chi \approx 0.35 \text{ cm}^{-1}$) and the alignment direction ($\chi \approx 70^\circ$) of the GO nanosheets (through equation S1a) for the unstirred solution.

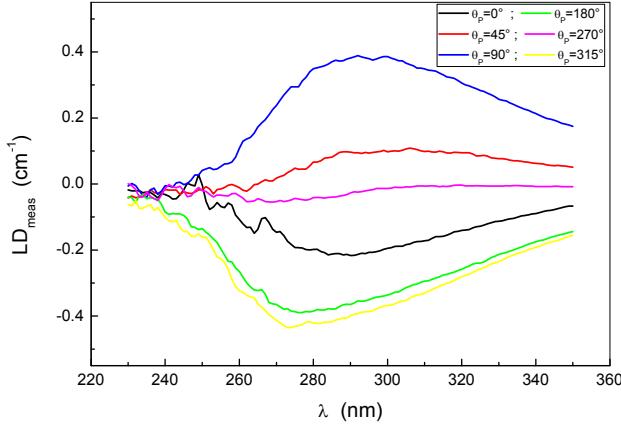


Figure S2: Typical LD spectra of a standing solution of GO at moderate concentration ($20 \text{ mg/L} < c < 50 \text{ mg/L}$).

The LD signals collected under CCW and CW vortexes are reported in figure S3 and S4, respectively, and indicate that the LD amplitude slightly decreases (with respect to the standing condition) to $LD_\chi \approx 0.15 \text{ cm}^{-1}$ for the CCW stirring sense, whereas it increases to $LD_\chi \approx 0.5 \text{ cm}^{-1}$ for the CW stirring sense. The alignment direction of the GO nanosheets becomes $\chi \approx 55^\circ$ and $\chi \approx 115^\circ$, respectively.

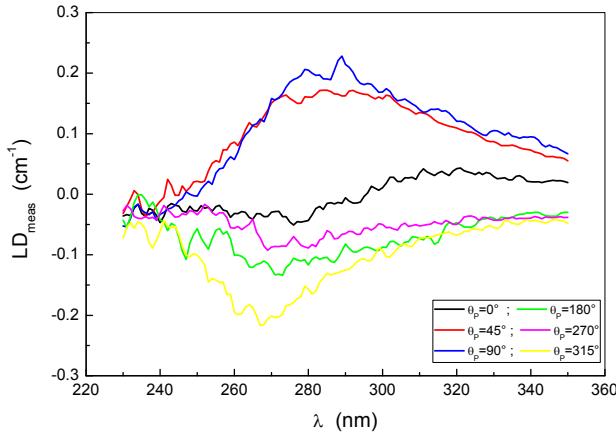


Figure S3: Typical LD spectra of a GO solution under CCW stirring at moderate concentration ($20 \text{ mg/L} < c < 50 \text{ mg/L}$).

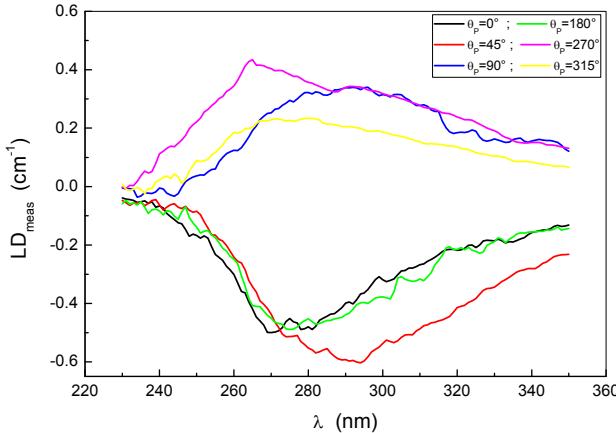


Figure S4: Typical LD spectra of a GO solution under CW stirring at moderate concentration ($20 \text{ mg/L} < c < 50 \text{ mg/L}$).

Upon further dilution (at the concentration of 10 mg/L) GO solution, besides not showing birefringence, exhibits a significantly lower LD signal (more than one order of magnitude lower), as shown in figure S5. From the LD magnitude at the wavelength of the absorption maximum, from the CD strength and from the linear birefringence of the optical system, due actually to the cuvette ($LB \approx 0.01$), it was calculated that the contribution of LD in the CD spectrum (cross-talk) is about 30% for the standing diluted solution and about 10% under stirring (data not shown).

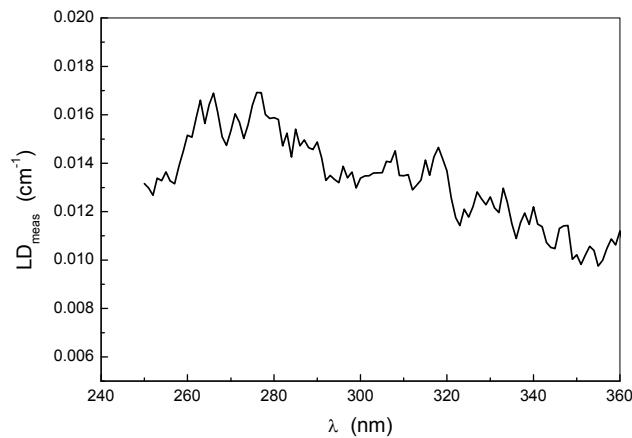


Figure S5: LD spectra of standing GO solution measured for $\theta_p=0^\circ$ at a concentration of 10mg/L.

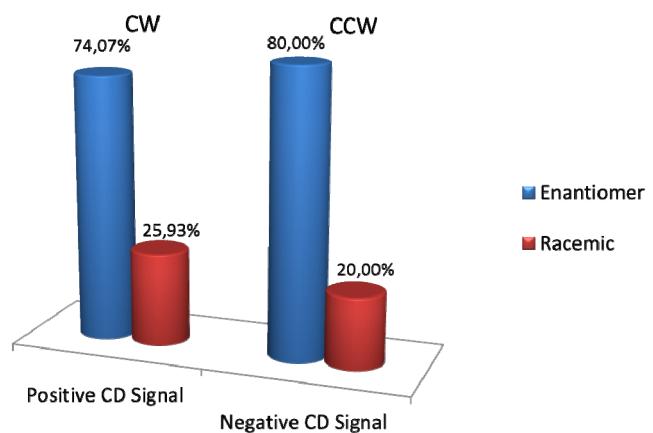


Figure S6. Statistical data of experiments. In order to verify the reproducibility of this simple chirality transfer method we have repeated it, different times. The statistics of these experiments, show that more than 70 % of the experiments led to the wanted result.

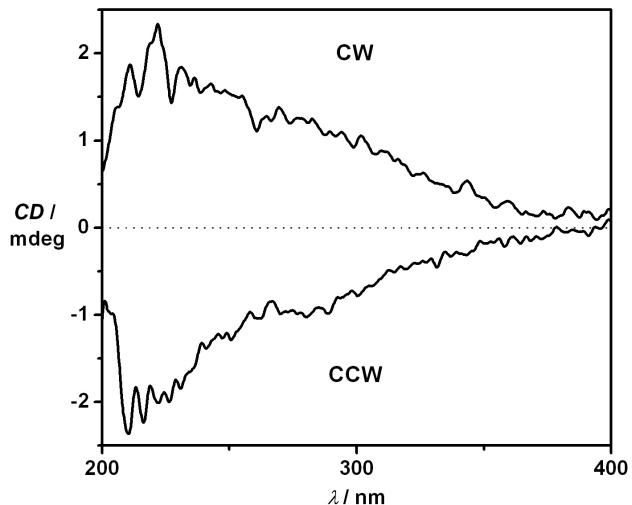


Figure S7. CD of quartz plates after drop casting of an aqueous GO solution deposited under CW and CCW stirring.

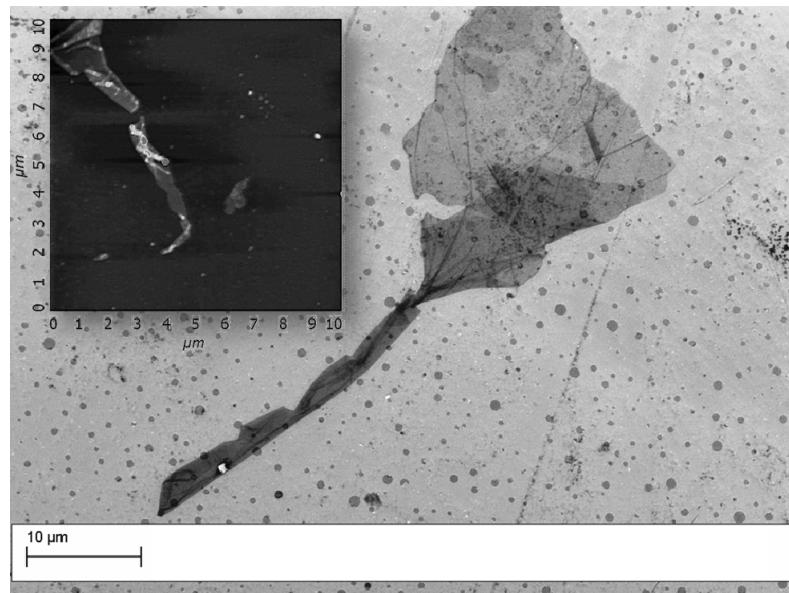


Figure S8: SEM image of GO folded single layer. AFM image of smaller nanostructure is shown for comparison (inset). These experiments are carried out on deposited GO by drop-CWstirring