

Second Harmonic Scattering from Mass Characterized 2D Graphene Oxide Sheets

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supplementary information

EXPERIMENTAL DETAILS

Materials

Graphite powder was obtained from Sigma-Aldrich. All the solutions were prepared using Millipore water (Milli Q system).

Synthesis of Graphene Oxide (GO)

Graphene oxide was synthesized using a modified Hummer's method. 3 g of natural graphite and 1.5 g of sodium nitrate were added to 69 mL of concentrated sulfuric acid and stirred in an ice bath for 30 minutes. 9 g of potassium permanganate was gradually added to the mixture while stirring maintaining the temperature below 20°C. Further the temperature of the mixture was raised to 35 °C and stirred for 12 hours.

138 mL of distilled water was added to the mixture, which raises the temperature up to 100 °C, after which stirring was continued for 2 hours.

Further, 30 mL of hydrogen peroxide (30%) was added dropwise until the colour of the mixture changes to bright yellow; after which the reaction is continued for 30 min.

Later, the reaction mixture was washed several times using 5% HCl to remove the sulphate salts and further was made alkaline by adding 5% Na₂CO₃. Finally, the alkaline reaction mixture

was filtered using filter paper and washed with water until it reaches its neutrality. The filtered solid GO was vacuum dried at 75 °C in an oven for 24 hrs to obtain a powdered form of GO.

Characterization

Mass measurements. Experiments were performed on a custom-built charge detection mass spectrometer with an electrospray ionisation (ESI) source (see figure S1 below).

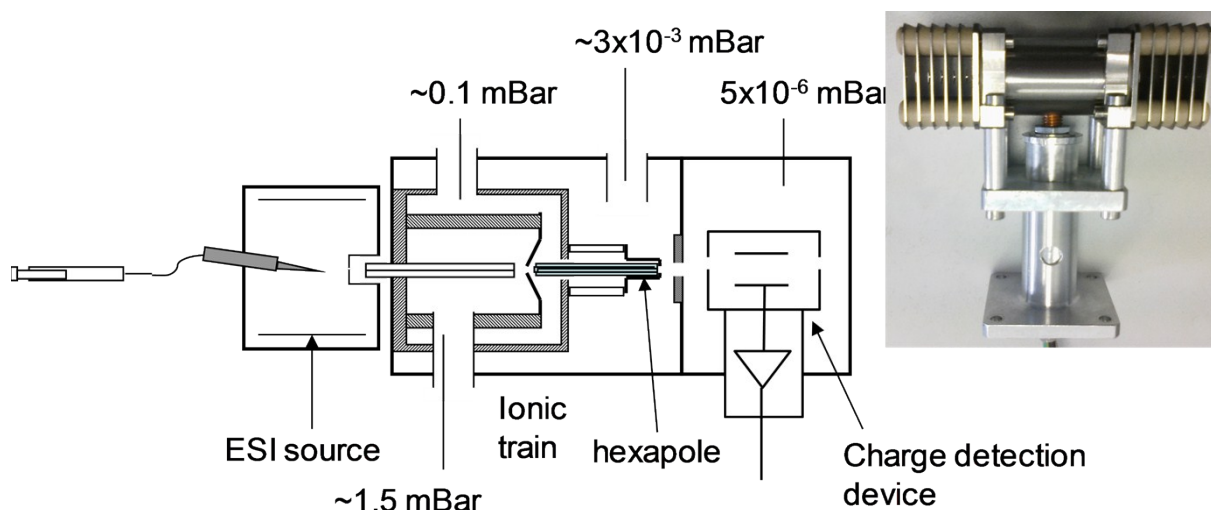


Fig. S1: Schematic view of a single pass charge detection set-up, comprising an ionization ESI source, an ionic train and a charge detection device. Inset : photograph of charge detection device.

The samples diluted in a water–methanol mixture (66.3/33.3 v/v) were injected at flow rates of typically 0.5 mL.h⁻¹, and entered the electrospray chamber through a 0.1 mm internal diameter stainless steel capillary tube located inside the needle tip. The MS signal obtained using a water–methanol mixture is dramatically increased as compared to pure water. Of note, the mass distribution obtained by electrospraying GO samples in pure water is close to the one reported for water–methanol mixture (data not shown). Nitrogen drying gas was injected between the end cap and the transfer glass capillary and flew through a heater typically set at 200 °C. The vacuum interface was composed of a glass transfer capillary that passes the ions into the first stage of the vacuum system, an end cap, a skimmer between the first and second vacuum stages, an hexapole ion guide and an exit lens. The charge detection device was used in a single pass mode. The signal induced on the tube was picked up by a junction gate field-effect transistor and was amplified by a low-noise, charge-sensitive preamplifier and then shaped and differentiated by a home-built amplifier. The signal was recorded with a waveform digitizer card that recorded the entire waveform for each ion passing through the detector tube at a sampling rate of 10 MHz. The data were transferred to a desktop computer where they were

analyzed to compute the charge and mass of each ion. Internal calibration in charge was performed using a test capacitor that allowed a known amount of charge to be pulsed onto the pick-up tube. Mass histograms are built from the collection of a statistically relevant number of single mass measurements for each sample (>2000 typically).

TEM. For transmission electron microscopy measurements, GO sample was drop-casted onto a silicon wafer. Conventional transmission electron microscopy (TEM) was conducted using a JEOL 2010 FTEM instrument.

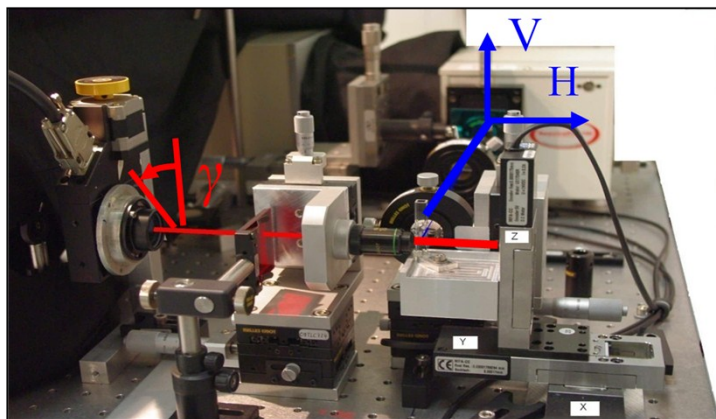
XPS. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a PHI Quantera SXM instrument (Physical Electronics, Chanhassen, USA) equipped with a 180° hemispherical electron energy analyzer and a monochromatized Al K α (1486.6 eV) source operated at 15 kV and 4 mA. The analysis spot had a diameter of 200 μ m and the detection angle relative to the substrate surface was 45°.

UV–visible measurements. UV–vis spectra in solution were recorded using an AvaSpec-2048 fiber optic spectrometer and an AvaLight-DH-S deuterium-halogen light source.

Nonlinear optical measurements. The set-up for hyperRayleigh scattering (HRS) and Multiphoton emission (MPE) has been described in details in previous works and is illustrated in Figure S2.¹⁻³ Briefly, the light source for the HRS and MPE measurements was a mode-locked femtosecond Ti: sapphire laser delivering at the fundamental wavelength of 800 nm pulses with a duration of about 140 fs at a repetition rate of 80 MHz. After passing through a low-pass filter to remove any unwanted harmonic light generated prior to the cell, the fundamental beam of about 400 mW was focused by a low numerical aperture microscope objective into a 0.5 cm spectrophotometric cell containing the aqueous solution. The HRS and MPEF light were collected at an angle of 90° from the incident direction with a 2.5 cm focal length lens. The HRS light was separated from the excitation light by a high-pass filter and a monochromator set at the harmonic wavelength. The HRS light was then detected with a photomultiplier tube (model H11890-210, Hamamatsu) working in the single photon counting regime.

For the MPE signal, the wavelength of the spectrometer (Jobin-Yvon, model iHR320) was scanned between 350 nm and 750 nm but the same detection unit was used.

Fig. S2: Photo of the classical 90° angle Hyper-Rayleigh scattering geometry. Two-photon excited fluorescence is also collected with the same geometry. Red line (excitation laser beam), blue line (photon detection).



1. I. Russier-Antoine, F. Bertorelle, R. Hamouda, D. Rayane, P. Dugourd, Z. Sanader, V. Bonacic-Koutecky, P.-F. Brevet and R. Antoine, *Nanoscale*, 2016, 8, 2892-2898.
2. I. Russier-Antoine, F. Bertorelle, M. Vojkovic, D. Rayane, E. Salmon, C. Jonin, P. Dugourd, R. Antoine and P.-F. Brevet, *Nanoscale*, 2014, 6, 13572-13578.
3. I. Russier-Antoine, F. Bertorelle, N. Calin, Z. Sanader, M. Krstic, C. Comby-Zerbino, P. Dugourd, P.-F. Brevet, V. Bonacic-Koutecky and R. Antoine, *Nanoscale*, 2017, 9, 1221-1228.

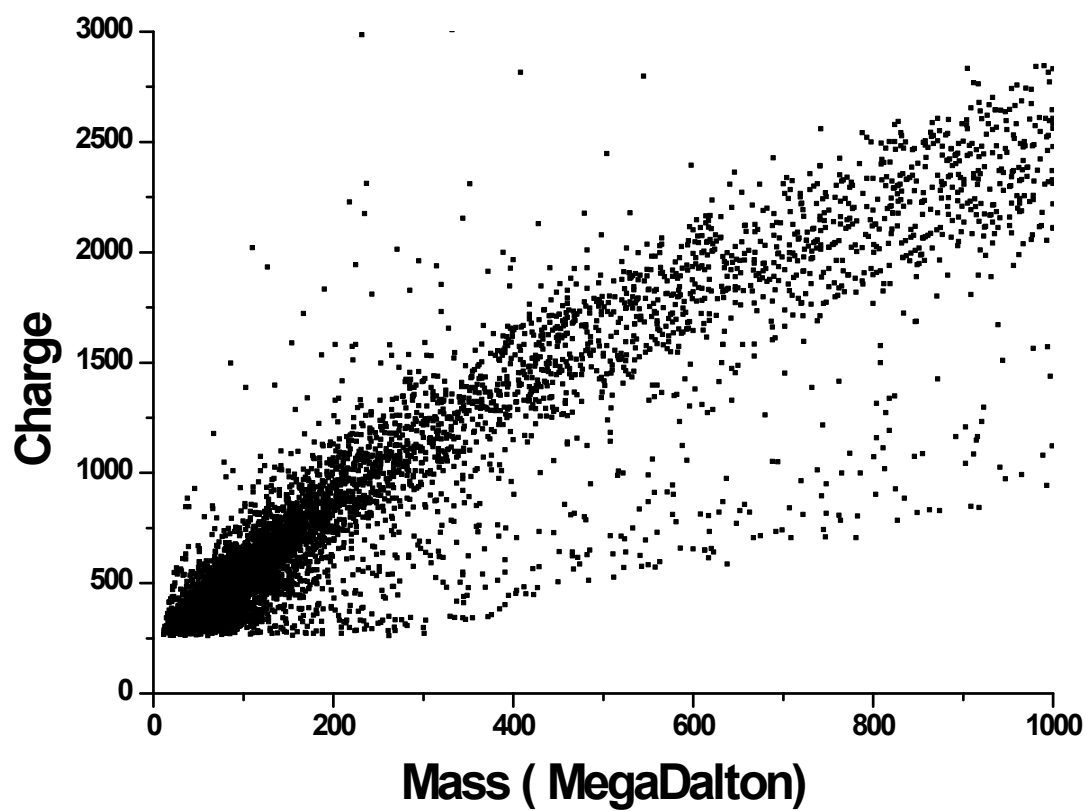


Fig. S3 : 2D charge - mass - image of individual ions from GO samples.

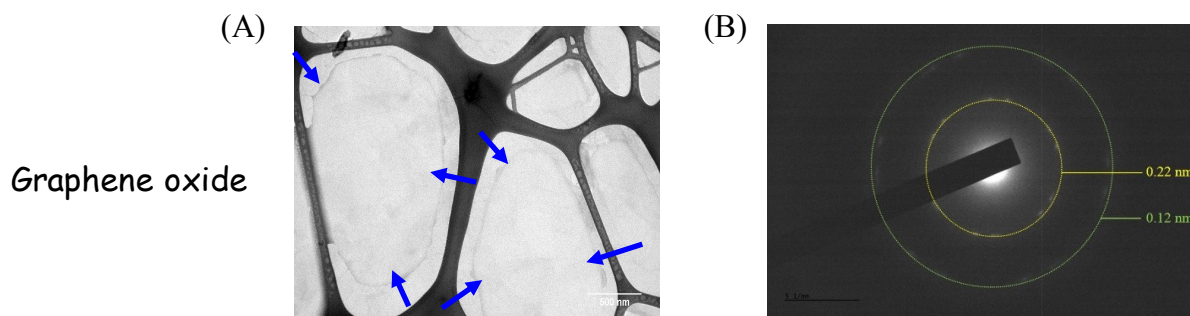


Fig. S4 : (a) TEM micrograph of graphene oxide nano sheets. Arrows are given for delineating GO sheets. (b) electron diffraction pattern from SAED measurements for graphene oxide sample.

Table S1 : Quantitative XPS results of as-prepared graphene oxide powder spectrum of which has been recorded in four subsequent measurements in order to determine the effect of X-ray irradiation on the chemical state of the sample.

	C	O	Na	S	Cl
Graphene Oxide					
(% content)	66	25	7	1.8	0.2

Table S2 : Analysis of C1s XPS peak of a graphene oxide (GO). The decomposition in curve components is shown in color scale underneath the data points in Fig. S6. The black line corresponds to the sum of all the individual components

	C-C/C-H	C-O	C=O	O-C=O
Graphene Oxide				
(% content)	67	18	9	6

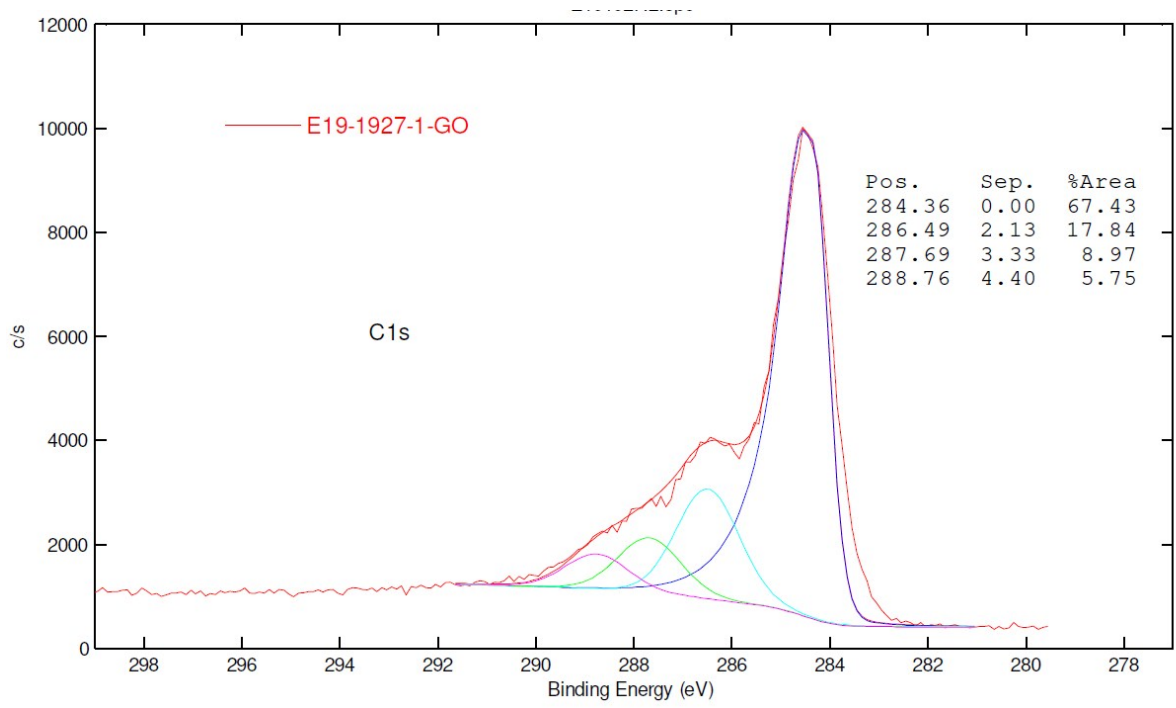


Fig. S5: C1s XPS peak of a graphene oxide (GO).

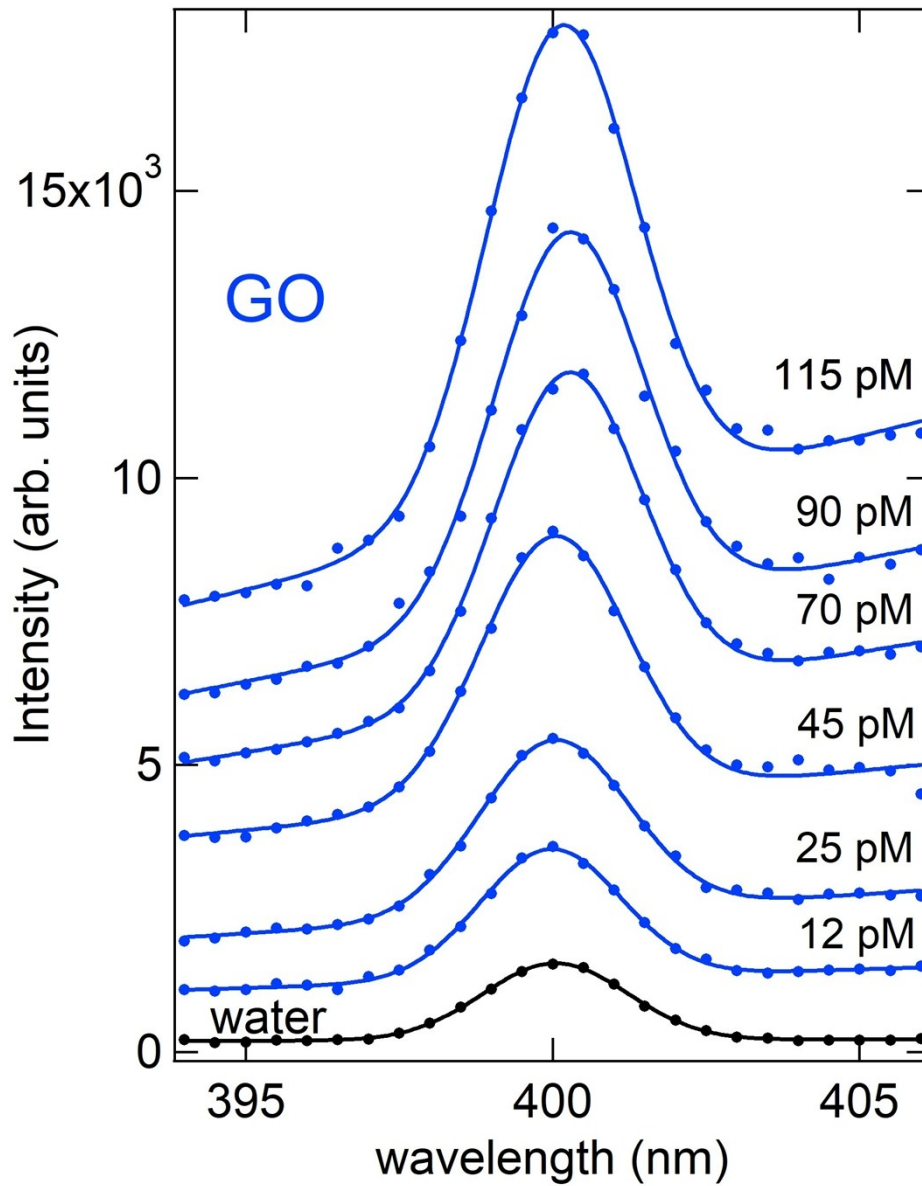


Fig. S6 : HRS intensity versus wavelength for GO solution of different concentrations. Lines : fit to a Gaussian function superposed on a linearly increasing function of the wavelength.

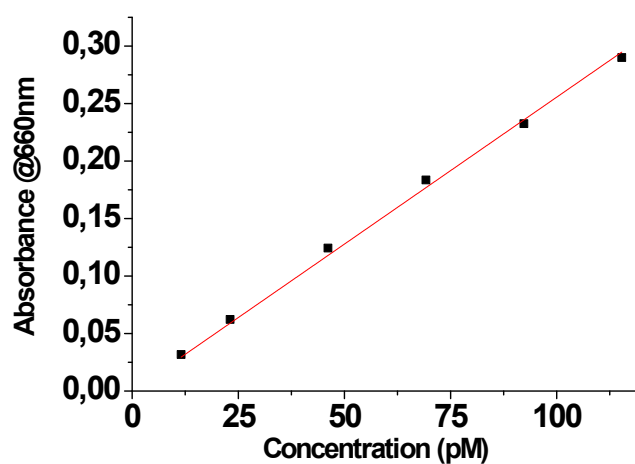


Fig. S7 : Dependence of the absorbance at 660 nm with concentration of graphene oxide in water. The linear fit is given (red line).

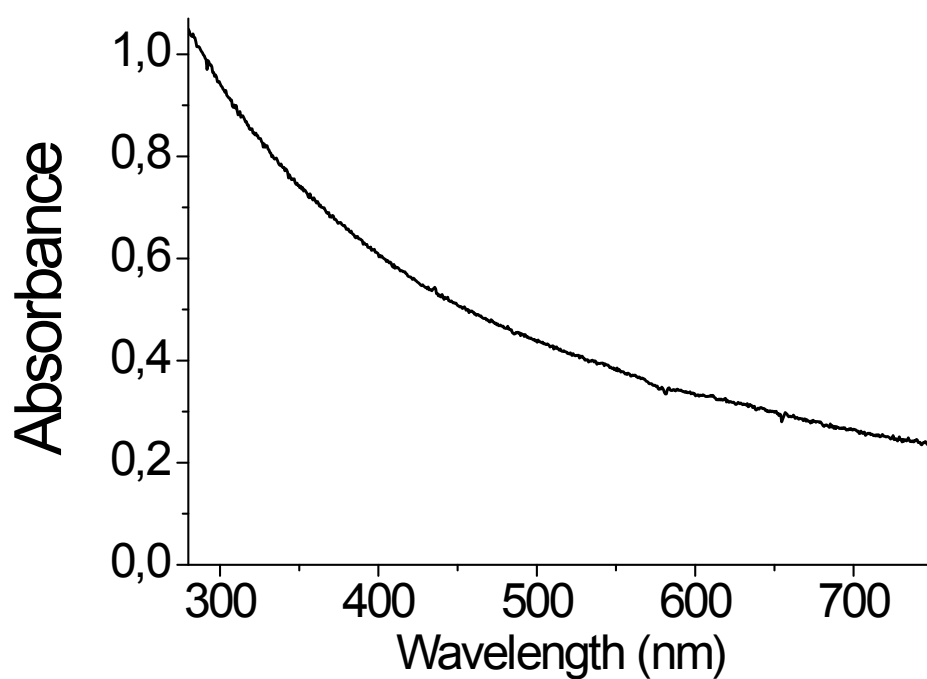


Fig. S8: UV-Vis absorption spectrum of GO in water at mass concentration of 8.07 mg/L.

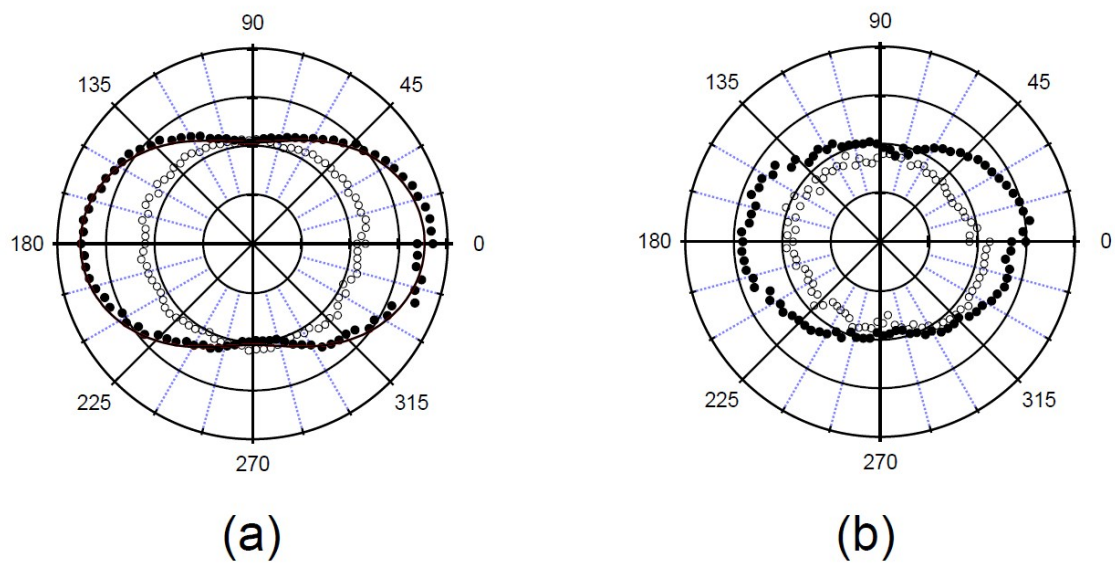


Fig. S9: Polar plots recorded at (a) 400 nm and (b) 390nm for horizontally (empty circles) and vertically (dark circles) polarized harmonic light for GO samples. The polar plot at 390 nm is used to subtract the fluorescence from the plot at 400 nm. GO in water at a concentration of 50 pM was used.

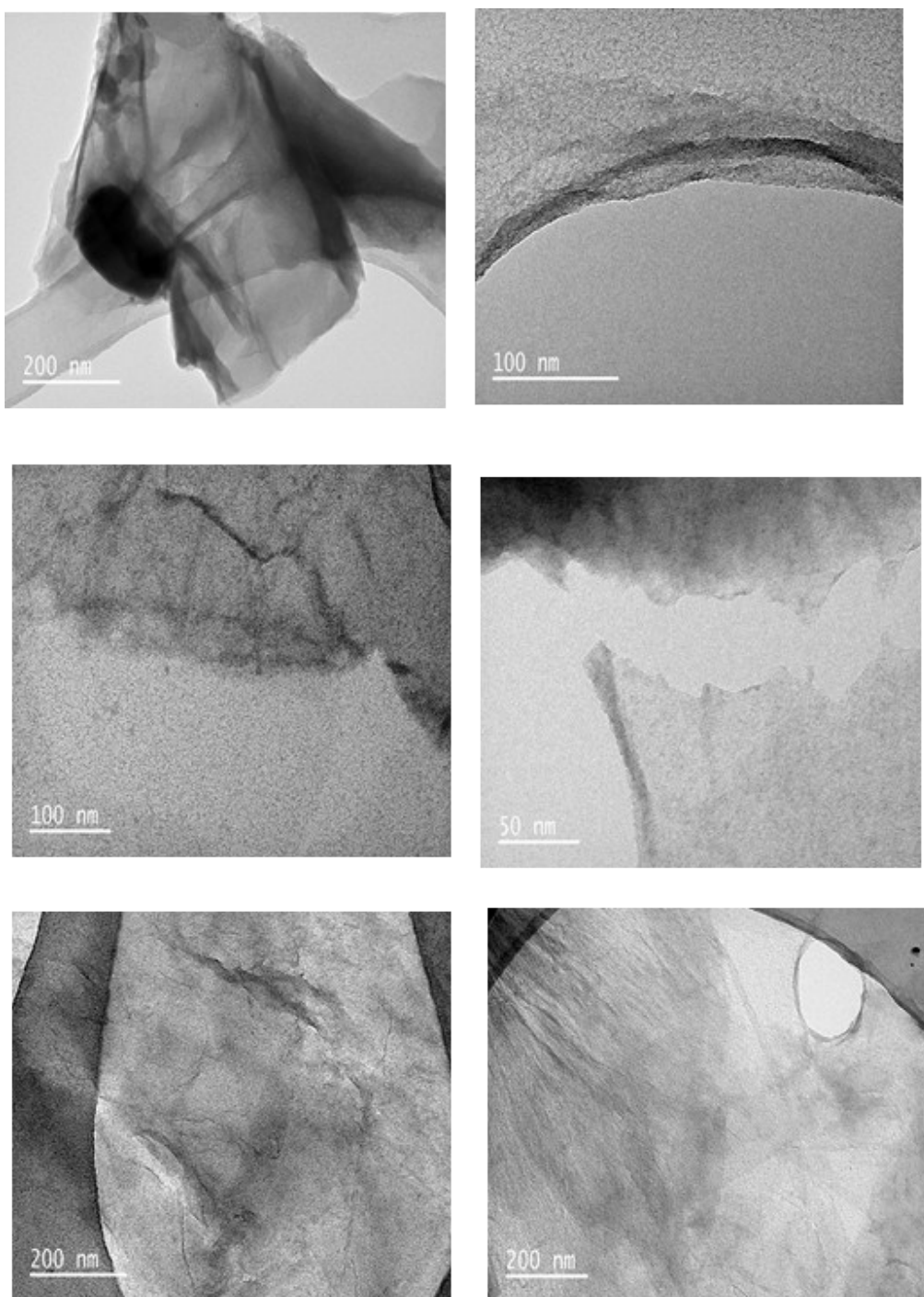


Fig. S10: Additional TEM images of graphene oxide nanosheets acquired over various areas of the TEM grid, showing the presence of wrinkled and wrapped nanosheets.