Supplementary information

Mechanochemical preparation of piezoelectric nanomaterials: BN, MoS_2 and WS_2 2D materials and their glycine-cocrystals

EXPERIMENTAL SECTION

Preparation of FLG and 2D nanomaterials

The synthesis of these nanomaterials through mechanochemical methods initiates using graphite obtained from Bay Carbon as precursor material, boron nitride, molybdenum disulfide and tungsten disulfide, all from Sigma Aldrich. Glycine was used as the exfoliating agents and was purchased from Sigma-Aldrich. In a typical experiment for the neat conditions, nanomaterials in raw and glycine (see table 1) were placed in a 250mL stainless steel jar containing 15 stainless steel balls (2 cm in diameter each). The jar was inserted in the planetary ball-milling machine (Retsch pm100) and the procedure was carried out at room temperature and air atmosphere for the required time (see table 1). After the milling treatment, the resulting solid mixtures were dispersed in 100mL of water. The resulting dispersions were dialyzed to remove the glycine in the media. The procedure consists in changing periodically the washing water while heating at 70ºC. It consists in one-over-night change and 5 changes every 90 min during the following day. The solutions were kept as stable dispersions at room temperature and air atmosphere. Dry powder samples are obtained after lyophilisation at −80 °C at a pressure of 0.005 bar.

Table S1. Comparison of effectiveness of method of synthesis.

Sample	Raw (mg)	Glycine (g)	Time, Rotational speed	Yield (%)	Average size (nm)
FLG1	75	0.25	2h, 100rpm	92.6	402.98±167
FLG2	75	4.5	4h, 250rpm	88.3	52.25±24
BN_{exfo}				77.2	172.4±55
$MoS_{2\ exfo}$	75	2.5	15min, 250rpm	82.9	290.23±114
$WS_{2\ exfo}$				86.5	302.45±107

Preparation of 2D nanomaterials-Glycine Cocrystals

In a typical experiment, raw materials (75 mg) and glycine (2.5g) were placed in a 250mL stainless steel jar containing 15 stainless steel balls (2 cm in diameter each). The jar was inserted in the planetary ball-mill (Retsch pm100) and the milling procedure was carried out at room temperature and air atmosphere for 15 min at 250rpm (except when starting from graphite that the milling took place during 2h). After the milling treatment, the resulting solid mixtures were dispersed in 100mL of water. Cocrystal dry powder were obtained after lyophilisation at −80 °C at a pressure of 0.005 bar.

CHARACTERIZATION TECHNIQUES

Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) data were recorded on a Philips (Panalytical) model X´Pert MPD diffractometer using Cu KAlpha1 (1.54056 Angstroms) at 40 kV and 40 mA. Diffraction patterns were collected over a range of 5–60° 2θ at a scan rate of 0.01° 2θ min^{-1} and a scan velocity of 0.004°s^{-1}.

Raman spectroscopy

Raman spectra were recorded on an InVia Renishaw microspectrometer equipped with 532 nm point-based laser. In all cases power density was kept below 1 mW μm^{-2} to avoid laser heating effects. Raman samples were measured in solid state under ambient conditions. The resulting spectra (after at least 30–40 random locations on each sample) were fitted with Lorentzian-shaped bands in their different peaks to ascertain band positions, widths and intensities.

Thermogravimetric analysis (TGA)

Thermogravimetric analyses (TGA) were performed with a TGA Q50 (TA Instruments) at 10 °C min^{-1} under nitrogen flow, from 100 °C to 800 °C.

Transmission Electron Microscopy (TEM)
TEM analyses were performed on stable dispersions of graphene (the same used for Raman analysis) diluted as necessary and dip-cast on Lacey copper grids (3.00 mm, 200 mesh), coated with carbon film, and dried under vacuum. The sample was investigated using a High-Resolution Transmission Electron Microscope (HRTEM) JEOL 2100 at an accelerating voltage of 100 kV.

X-ray photoelectron spectroscopy (XPS)
XPS measurements were performed in a SPECS Sage HR 100 spectrometer with a nonmonochromatic X ray source of Aluminium with a Kα line of 1486.6 eV energy and 300 W. XPS measurements were performed in a SPECS Sage HR 100 spectrometer with a nonmonochromatic X ray source of Aluminium with a Kα line of 1486.6 eV energy and 300 W. The e XPS data were analyzed using CasaXPS software.

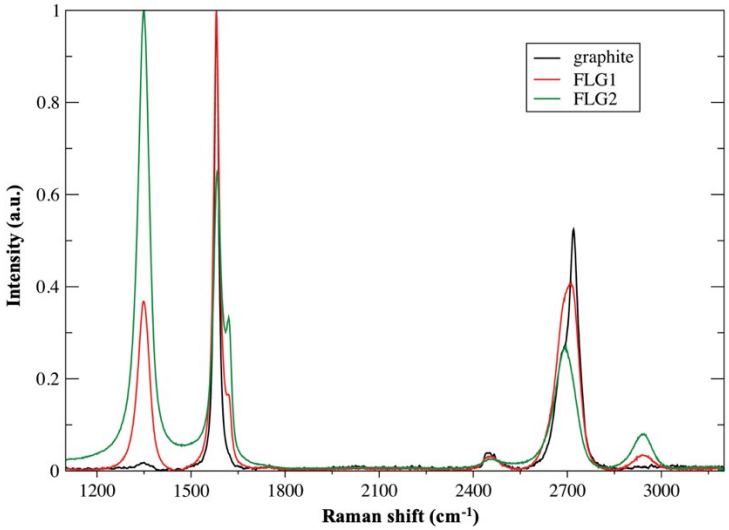


Figure S1. Raman spectra for FLG prepared with glycine at two different conditions (FLG1 and FLG2) by ball milling.

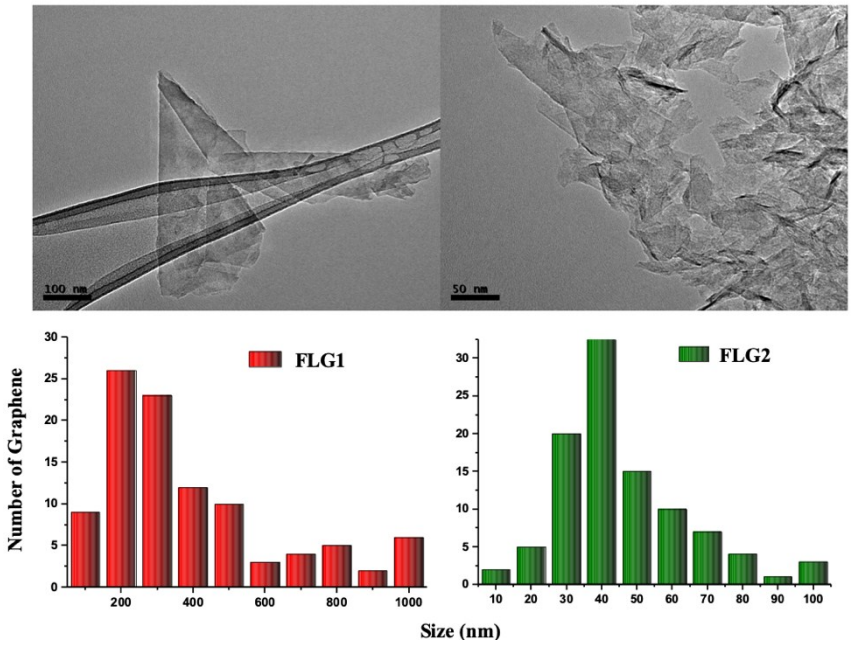


Figure S2. TEM of nanomaterials with FLG1 and FLG 2 distributions

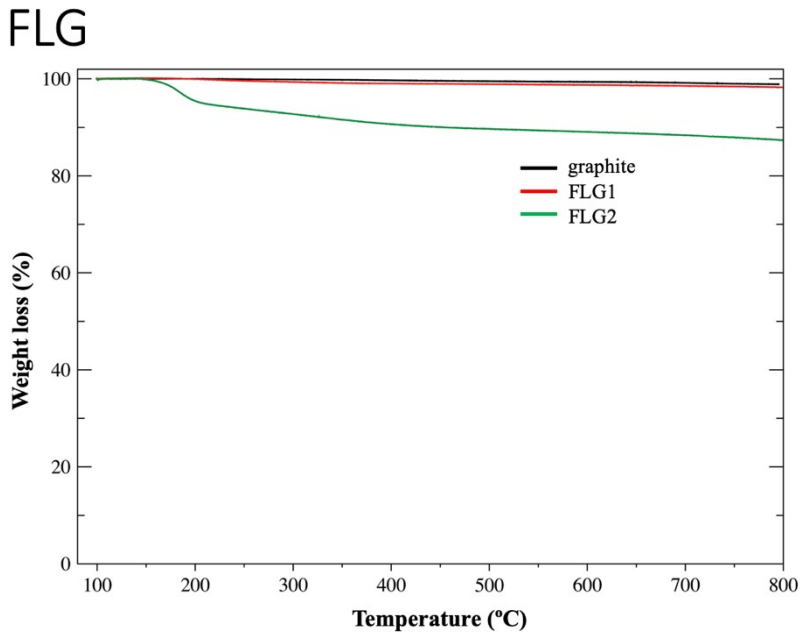


Figure S3. Thermogravimetric analysis (TGA) of FLG1 and FLG2.

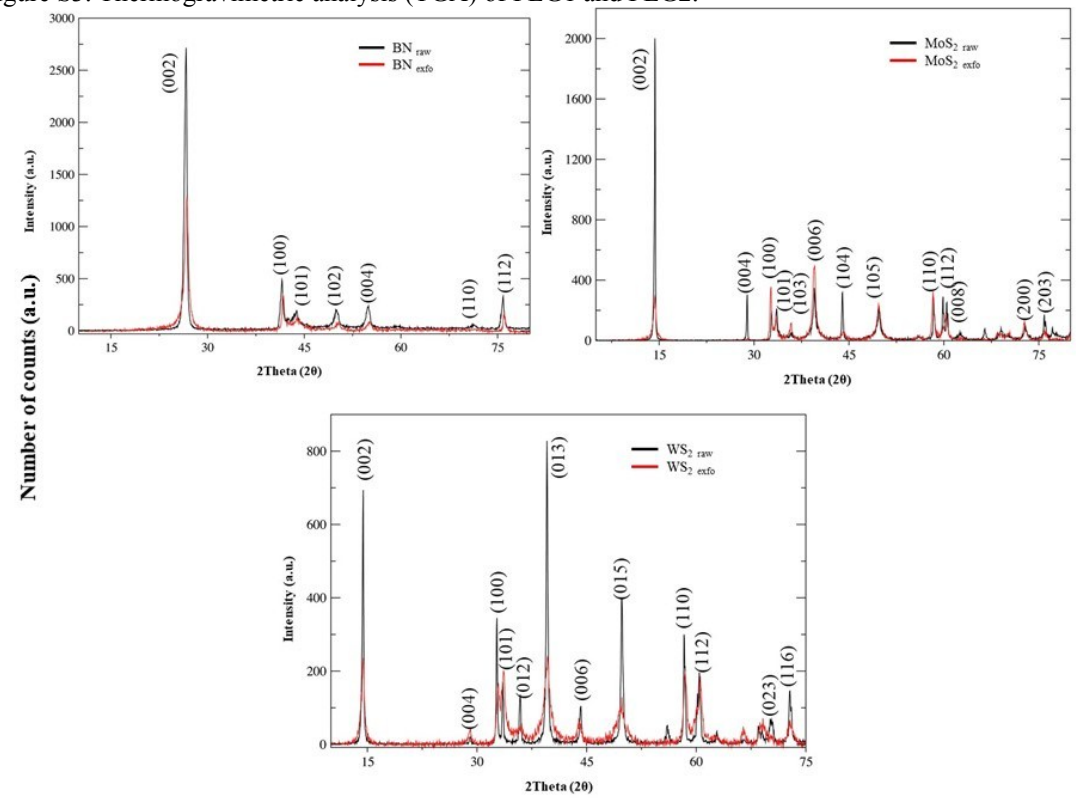


Figure S4. Comparison of Powder X-Ray Diffraction (PXRD) from raw and exfoliated nanomaterials.”.

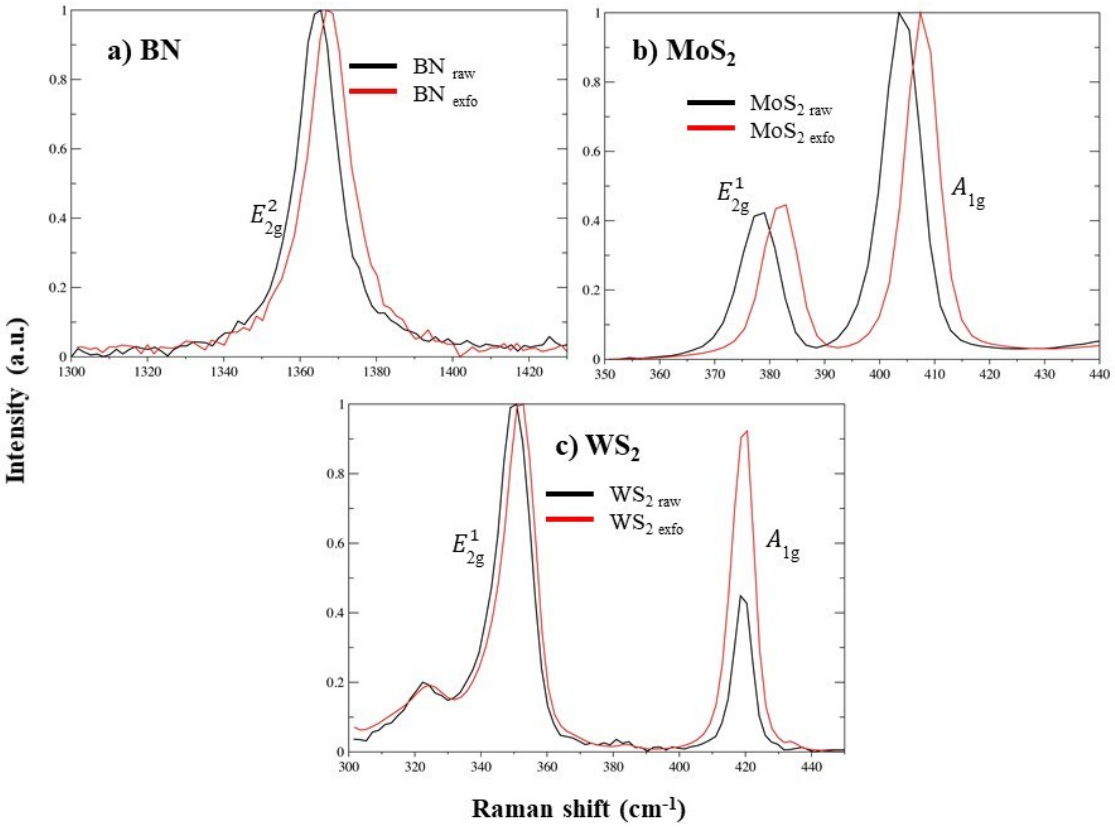


Figure S5. Raman spectra for 2D nanomaterials prepared with glycine by ball milling.

Table S2. Raman data for the 2D nanomaterials exfoliated materials.

Sample	Main peak (MP, cm^{-1})	Intensity	Secondary peak (SP, cm^{-1})	Intensity	Raw-Exfo. Shift (cm^{-1})	MP-SP Shift (cm^{-1})	Ratio MP/SP
BN raw	1364.55 (E^2_{2g})	1.02	--	--	--	--	--
BN exfo	1367.53 (E^2_{2g})	1.01	--	--	2.98	--	--
MoS_2 raw	378.05 (E^1_{2g})	0.40	403.96 (A_{1g})	0.92	--	25.91	0.44
MoS_2 exfo	380.04 (E^1_{2g})	0.40	405.83 (A_{1g})	0.87	MP (1.99), SP (1.87)	25.79	0.46
WS_2 raw	349.95 (E^1_{2g})	0.83	420.67 (A_{1g})	0.19	--	70.72	4.51
WS_2 exfo	351.38 (E^1_{2g})	0.70	417.93 (A_{1g})	1.02	MP (1.43), SP (-2.74)	66.55	0.69

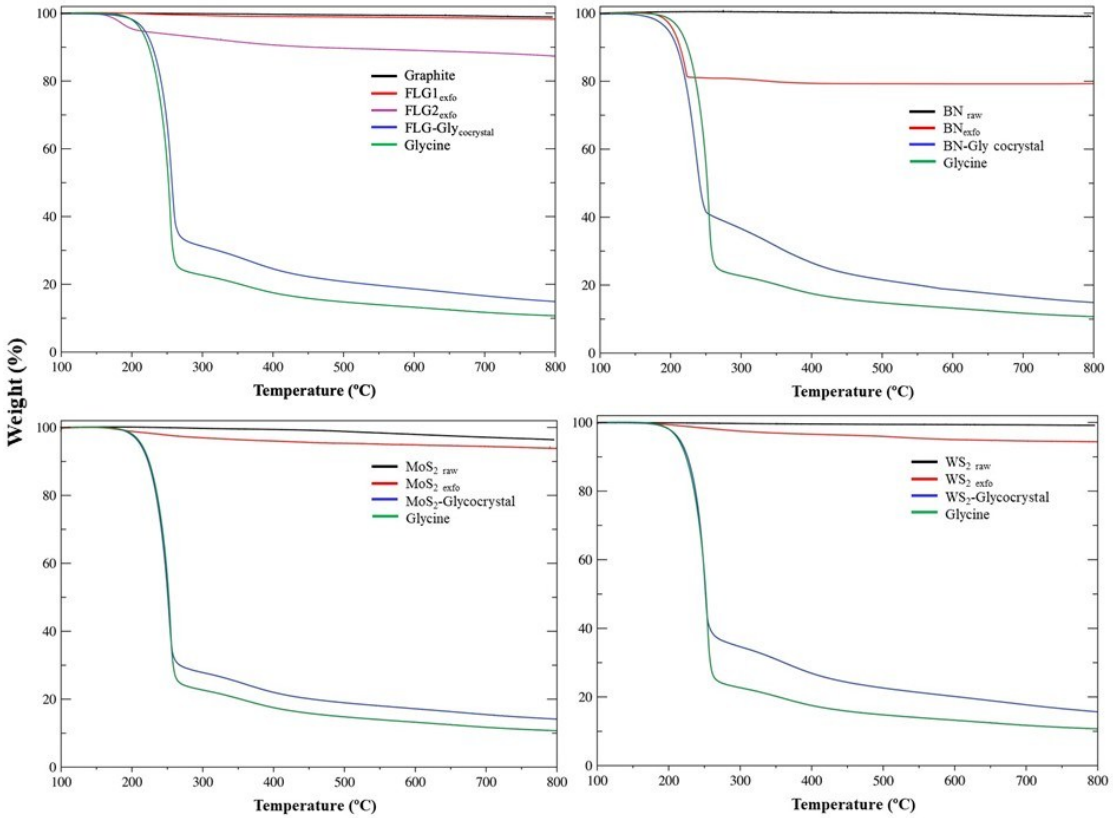


Figure S6. Thermogravimetric analysis (TGA) of the different 2D nanomaterials in raw, exfoliated 2D nanomaterials and 2D nanomaterial-glycine cocrystals in comparison with glycine.

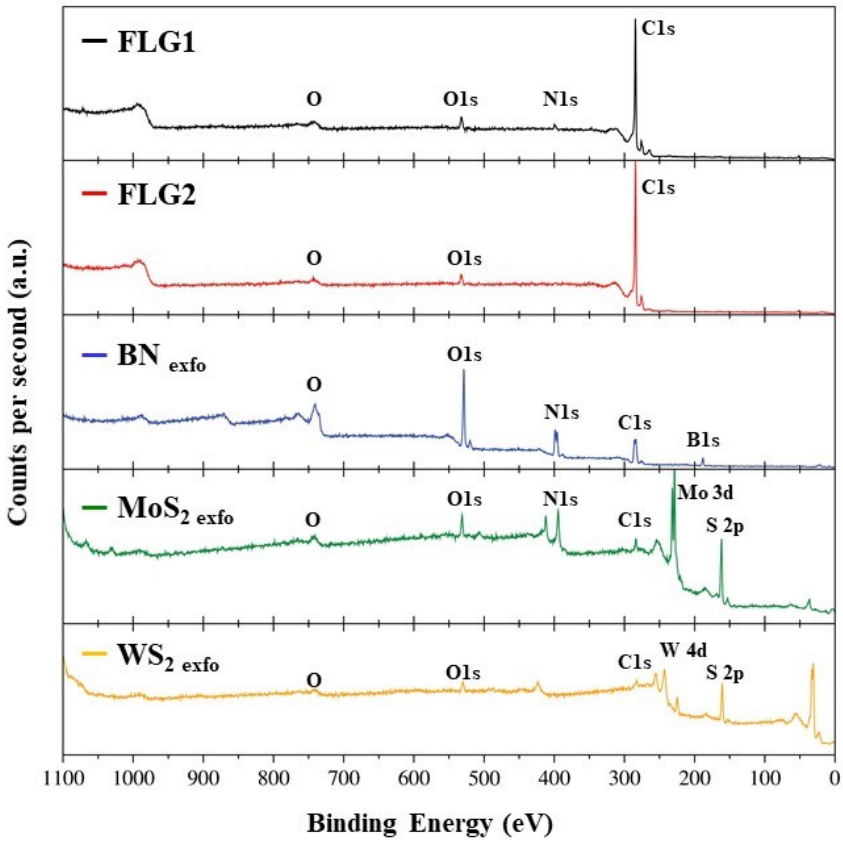


Figure S7. Wide scan XPS spectra for the 2D layered nanomaterials samples.

Table S3. XPS atomic content (%) of the 2D nanomaterials samples.							
Sample	**%C**	**%O**	**%N**	**%S**	**%B**	**%Mo**	**%W**
FLG1	93.1	4.9	2.0	-	-	-	-
FLG2	96.3	3.4	0.3	-	-	-	-
BN_{exfo}	36.0	26.7	24.7	-	12.6	-	-
$MoS_{2\ exfo}$	15.4	11.7	traces	46.7	-	26.2	-
$WS_{2\ exfo}$	18.1	11.4	-	46.3	-	-	24.2

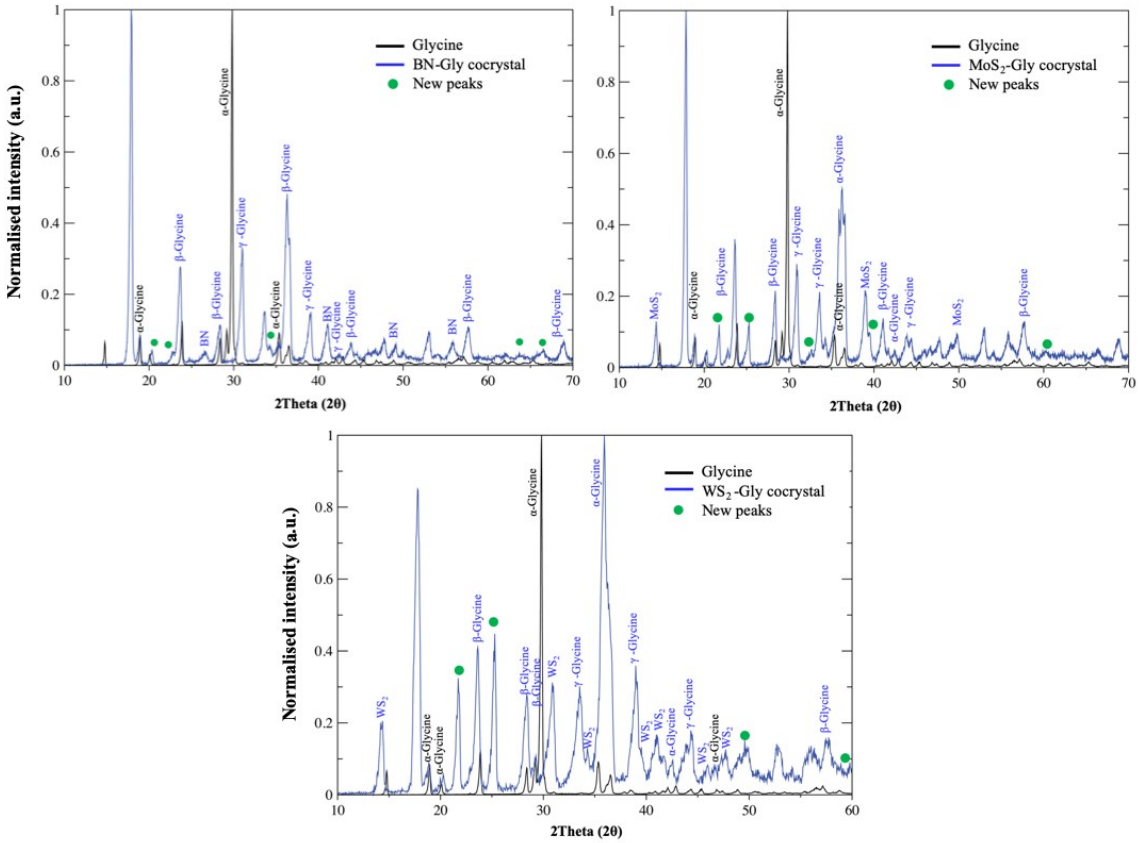


Figure S8. Comparison of PDXR from 2D nanomaterials cocrystal structures and starting glycine.

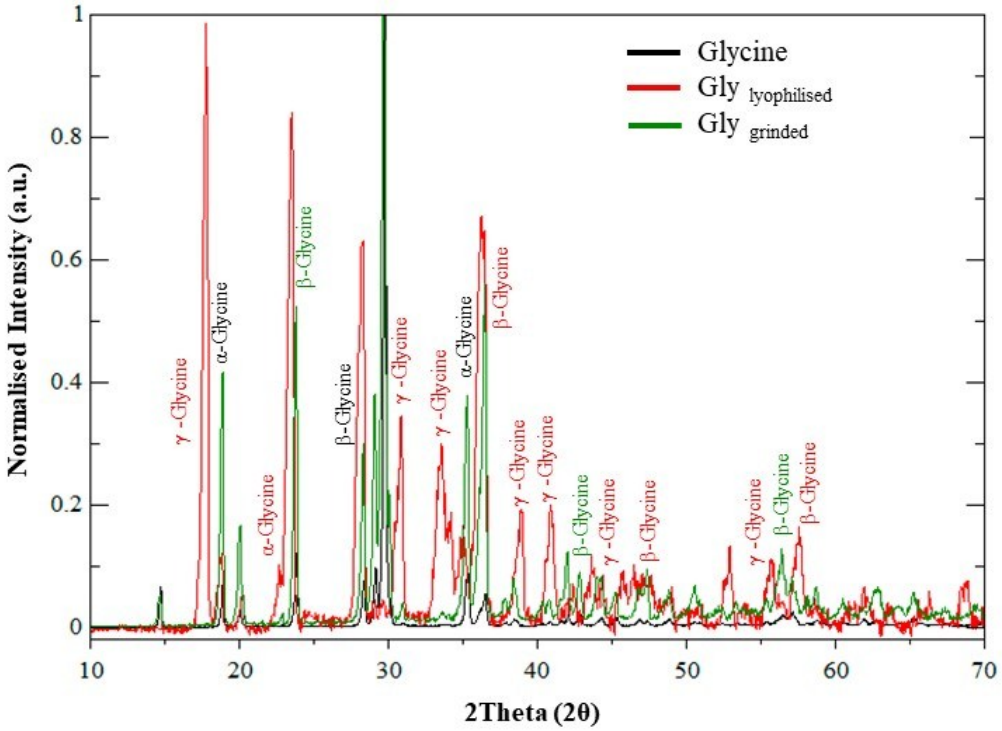


Figure S9. Powder X-ray diffraction results for glycine commercial, cocrystal and grinded.

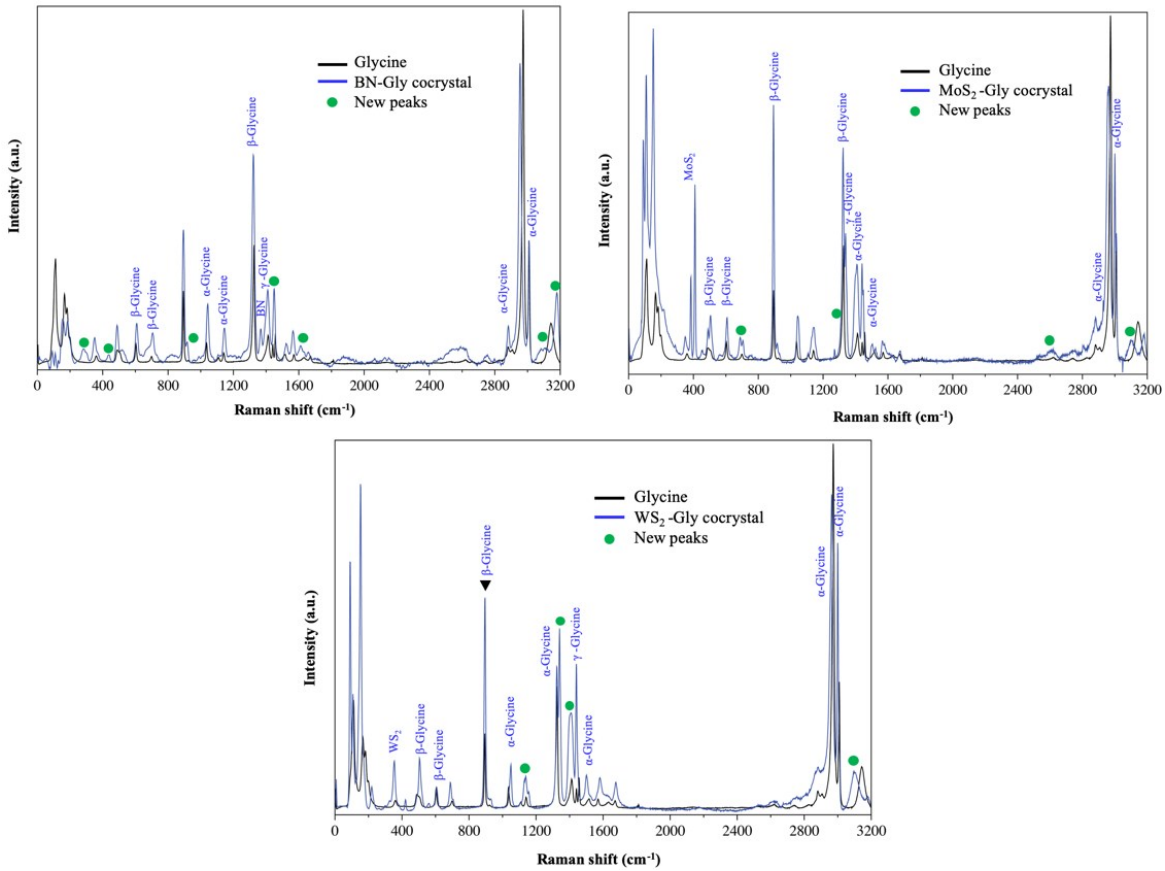


Figure S10. Comparison of Raman spectra from 2D nanomaterials cocrystal structures and starting glycine.

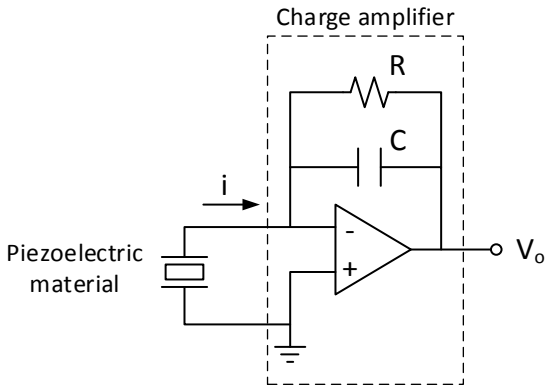
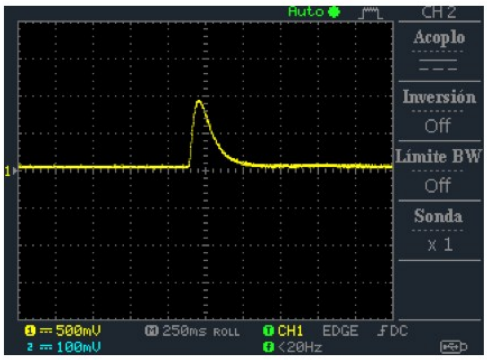


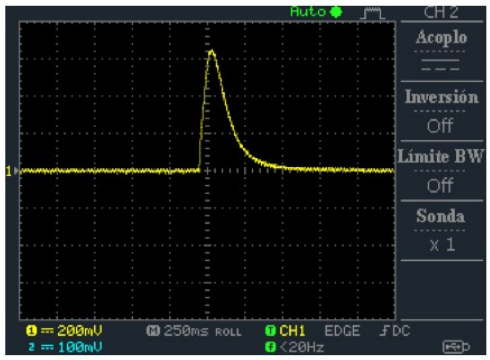
Figure S11. Schematic representation of the open circuit used in this work.

ΔF=10N

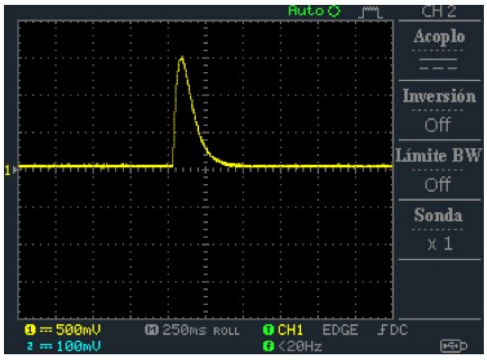
FLG-Gly cocrystal



BN-Gly cocrystal



MoS_2-Gly cocrystal



WS_2-Gly cocrystal

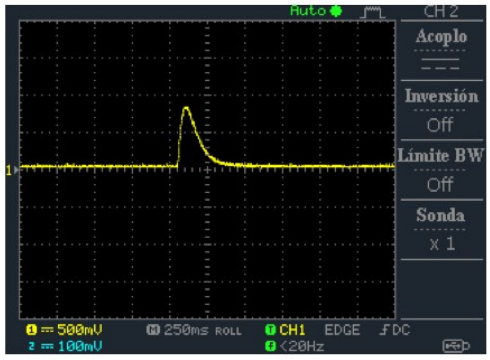


Figure S12. Comparison of piezoelectricity response of 2D nanomaterials cocrystal with glycine

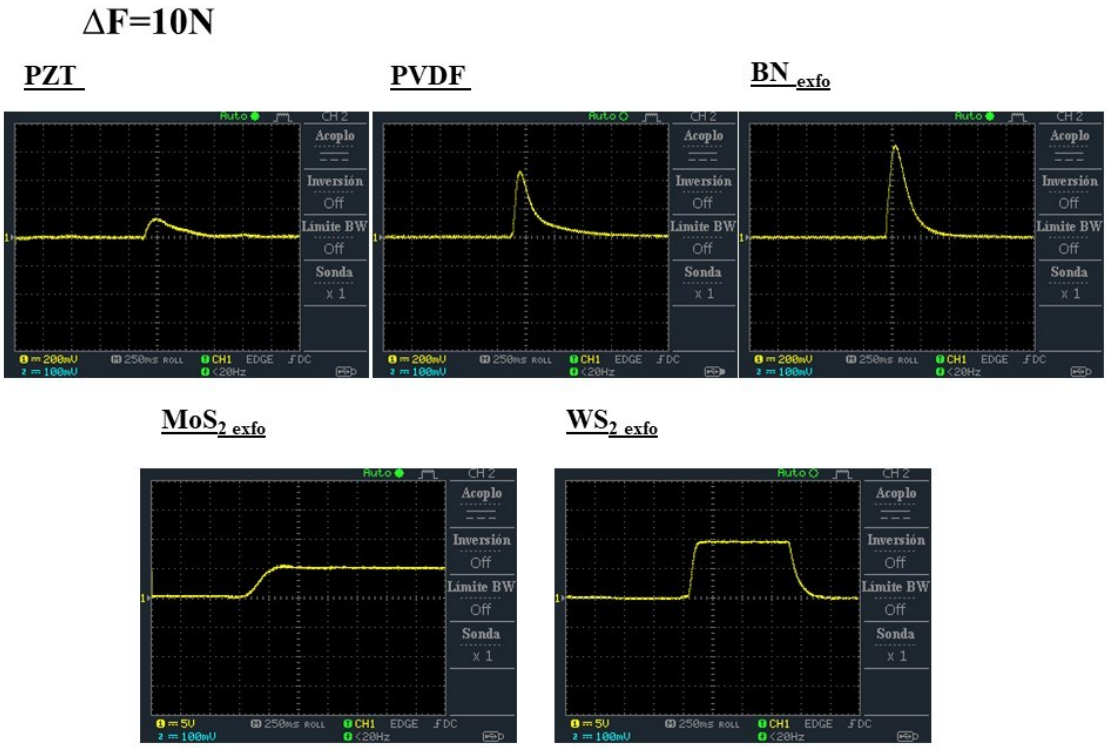


Figure S13. Comparison of piezoelectricity response of exfoliated 2D nanomaterials with glycine and PZT.

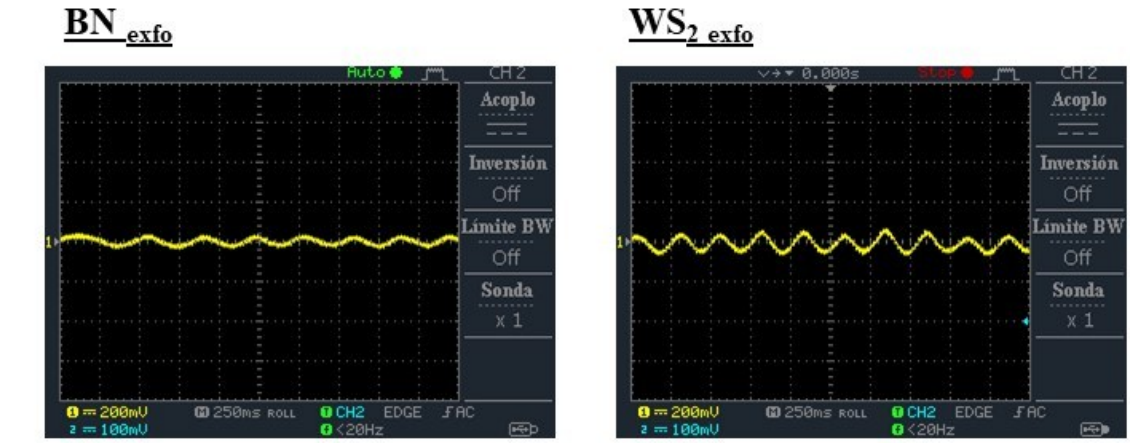


Figure S14. Piezoelectricity response of BN and WS_2 exfoliated were responsive enough to produce a recovery cycle maintain in time