Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

High power mechanical energy harvester based on exfoliated black phosphorous - polymer composite and its multiple applications

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Experimental Methods:

Black Phosphorus (BP) nanosheets exfoliation: BP crystals (200 mg) were treated well in stiff powder with mortar and pestle inside the glove box. The resultant powder was dissolved in 100 ml of N-Methyl-2-pyrrolidone (NMP) immediately. With the help of Probe sonicator (Vibra Cell, VCX-500W, Sonics Inc, USA), the mixture was sonicated for 6 hrs with 40% amplitude for cycle run (5s and 5s off) within temperature range 4-8 ^{o}C. For removing of un-exfoliated BP crystals, sonicated BP/NMP dispersion was relaxed for few hours, and by gravity, un-exfoliated BP crystals were settled down. The supernatant was transferred into Centrifuge subsequently. At a speed of 1000 rpm for 3 hrs, centrifugation removed the remaining exfoliated BP crystals. BP/NMP dispersion was collected again from top 60% of the supernatant from centrifuge tubes. The last supernatant was centrifuged at a speed of 6000 rpm for 60-80 min, and again 80% supernatant was easily pipetted out to remove junk BP. The sediment was re-dispersed in NMP solution for further piezoelectricity application part.

Fabrication of the flexible piezoelectric composite NG and testing:

The initial device only BP nanosheet based PENG is fabricated by directly drop casting of BP/NMP dispersion on Au/Cr coated Polyethylene Terephthalate (PET) in the glove box and heated at 80^{o}C for 5 hrs to dry up the BP film. After drying the BP film, another set of Au/Cr coated PET is put on BP film and device is sealed through Araldite.

For the fabrication of Polydimethylsiloxane **(**PDMS**) -** BP nanosheets based piezoelectric NG, the exfoliated black phosphorus nanosheets were mixed with 3 ml of PDMS in different weight ratio 0.1%, 0.15%, 0.2% and 0.3%. The resulted composite solution was drop cast onto the Au/Cr coated PET substrate and cured at 90^{o} C temperature. After 3 hours, other Au/Cr coated PET substrate as a top electrode was assimilated to cured composite layer. In result, BP-PDMS composite layer was sandwiched between a/cr coated PET. After that we sealed device with Kapton tape such that there should not be any friction between gold and the BP-PDMS surfaces.The dimension of flexible piezoelectric nanogenerator was 2×2 cm^2. For Force source, we assembled a 50 g weight (area 5 cm^2) to the edge of sewing to get the continuous impact. An impact force from the sewing machine was used to obtain 40 to 45 N force at a frequency of 25 Hz on the device with PASPORT Force Sensor. The voltage generated by BP device is used for charging the 2.2µF capacitor through bridge rectifier circuit. The stored charge is used to light up the LED by using a bridge rectifier. Change in capictance of devices is measured by Keithley DMM7510 7.5 multimeter. All Output voltage and current measurements are recorded on Tektronix Oscilloscope MSO 2024 and Keithley DMM7510 7.5 multimeter.

Characterization techniques:

***Field emission scanning electron microscopy (FE-SEM)**:* Zeiss Ultra Plus FESEM at 5-10 kV was used for SEM imaging. Only black phosphorus and BP-PDMS film were prepared by drop casting on glass substrate.

***Transmission electron microscopy (TEM)**:* TEM imaging was performed by using JEM2200FS TEM microscope at 30-200kV.

Atomic Force Microscopy: Agilent Technologies 5500 AFM instrument was used to observe thickness of single BP nanosheet. BP nanosheet sample was prepared by drop casting BP/NMP solution on glass substrate.

X-ray diffraction (XRD): All XRD data were collected on Bruker D8 Advance diffractometer using Cu Kα radiation (λ = 1.5406 A).

Piezoelectric Force Microscopy (PFM) measurement details:

The polarization switching and local piezoelectric response of BP nanosheets were studied at room temperature with an Asylum Research MFP-3D atomic force microscope working in contact mode. An ASYLEC-01 cantilever made of a tetrahedral silicon tip coated with titanium / Iridium (5/20) was used to apply a small A.C. voltage with amplitude of 600 mV. Measurements were performed by applying two oscillating voltages with frequencies below and above resonance (270 kHz), operating the cantilever in the dual a.c. resonance tracking mode. The solution was drop casted on 1cm X 1cm FTO coated glass slide and annealed for 30 min at 180º C inside the N_2 filled glove box.

Computational Details

We performed density functional theory calculations within the projector augmented wave formalism [1] with a plane-wave cutoff of 400 eV as implemented in Vienna Ab initio Simulation Package (VASP).[2,3] The exchange-correlation was described with the Perdew-Burke-Ernzerhof form of generalized gradient approximation.[4] The monolayer phosphorene was modeled using a 2x2 supercell. The periodic images were separated by a vacuum of 15 Å. The reciprocal space integrations were carried out using $11 \times 8 \times 1$ Monkhorst-Pack k-points, and the full structural optimizations were carried until the energy and force components are below a threshold of 10^{-6} eV and 5×10^{-3} eV/Å, respectively.

References and notes

1. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, 50,17953– 17979
2. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, 47, 558– 561
3. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, 54, 11169– 11186
4. *Phys. Rev. Lett.***1996**, 77, 3865– 3868

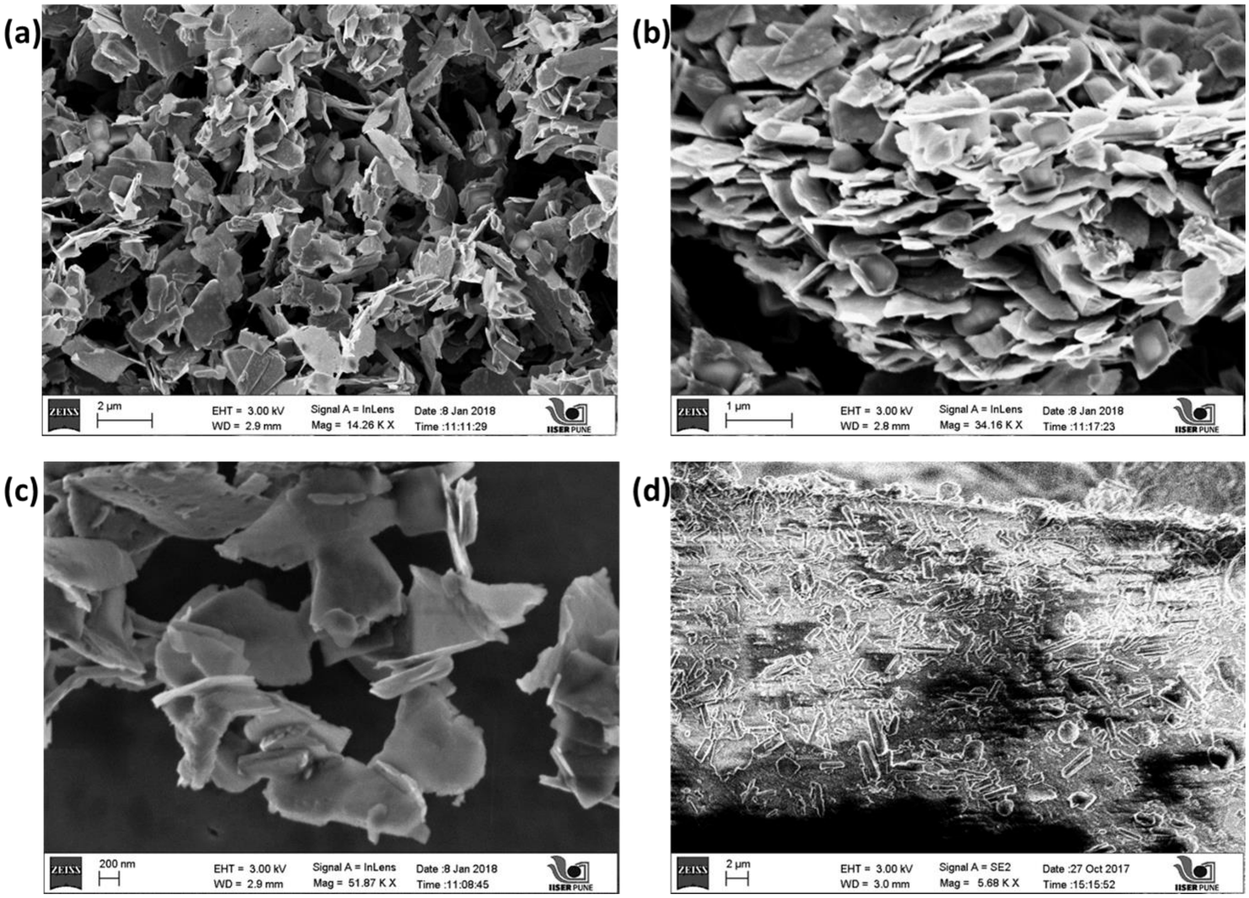

Figure S1 SEM images of BP nanosheets **(**a**)**, **(**b**)** and **(**c**)** show uniform lateral size of BP nanosheets synthesized by the Probe sonication method and (d) Cross-sectional SEM image of PDMS-BP nanosheet composite film which showshomogeneous encapsulation of BP nanosheets in PDMS matrixs.

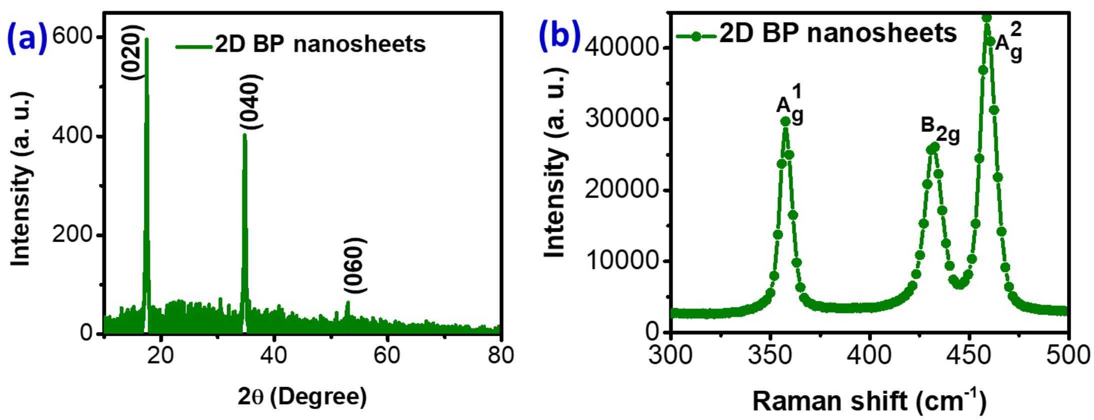

Figure S2 Basic characterization of BP nanosheets: **(**a**)** Powder XRD of BP nanosheets, all peaks show corresponding Orthorhombic phase of BP, and **(**b**)** Raman spectrum shows the expected signature peaks of BP**.**

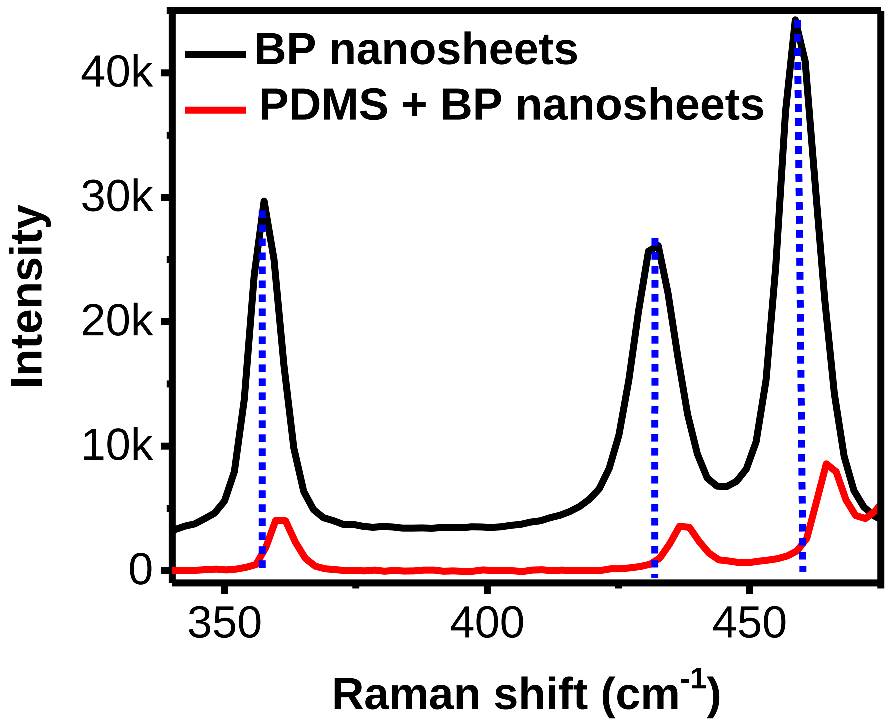

Figure S3 Comparison of the Raman spectra of BP nanosheets and PDMS-BP nanosheets composite shows that all the Raman modes in the case of the composite are shifted to higher wavenumbers with reference to the BP nanosheets case**.**

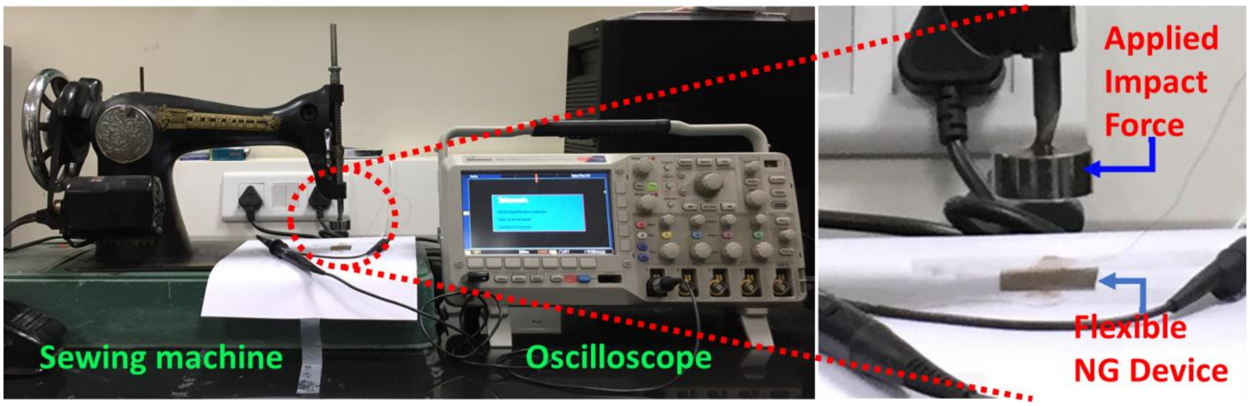

Figure S4 Impact Force set-up: Sewing Machine Set up to get constant impact force of 40N and Oscilloscope to measure output performance. Inset shows the changes in sewing machine for constant impact.

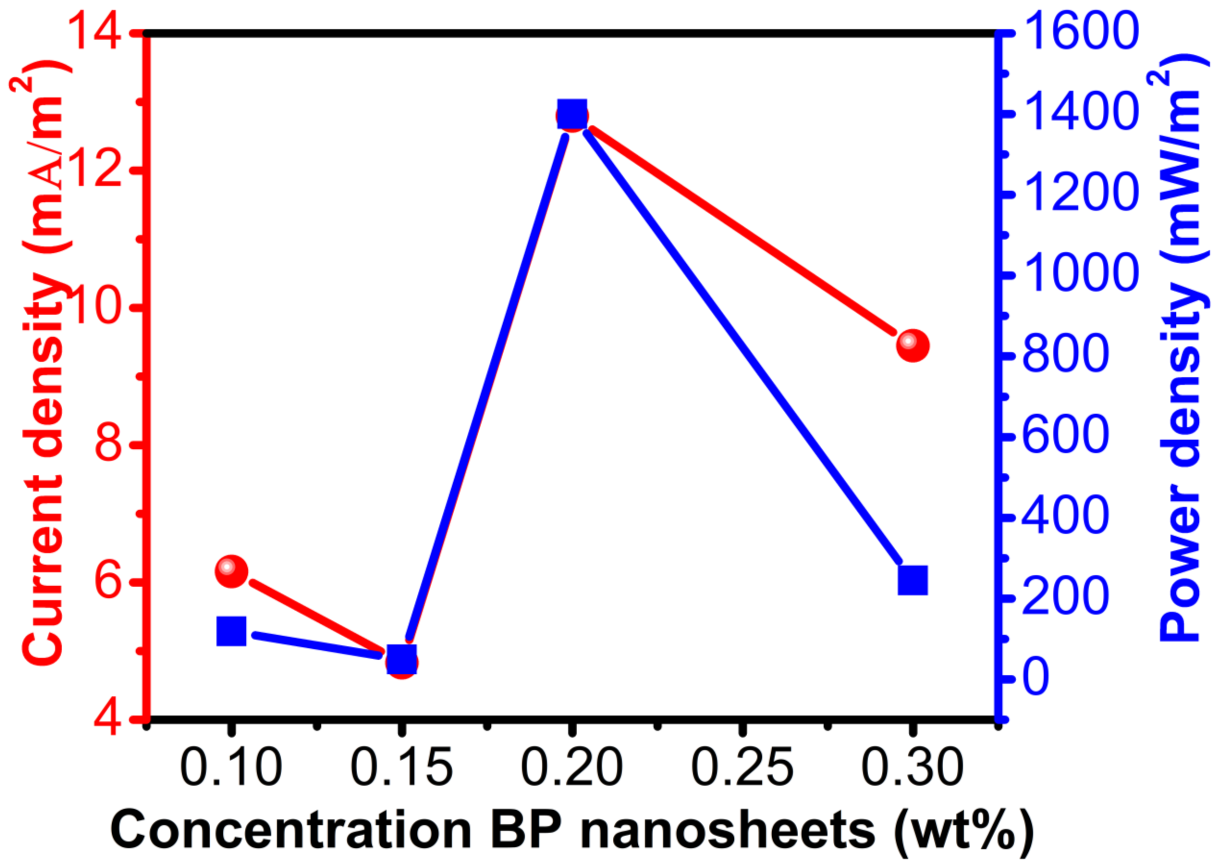

Figure S5 Maximum current density and power density of flexible NG device with different concentrations (wt%)

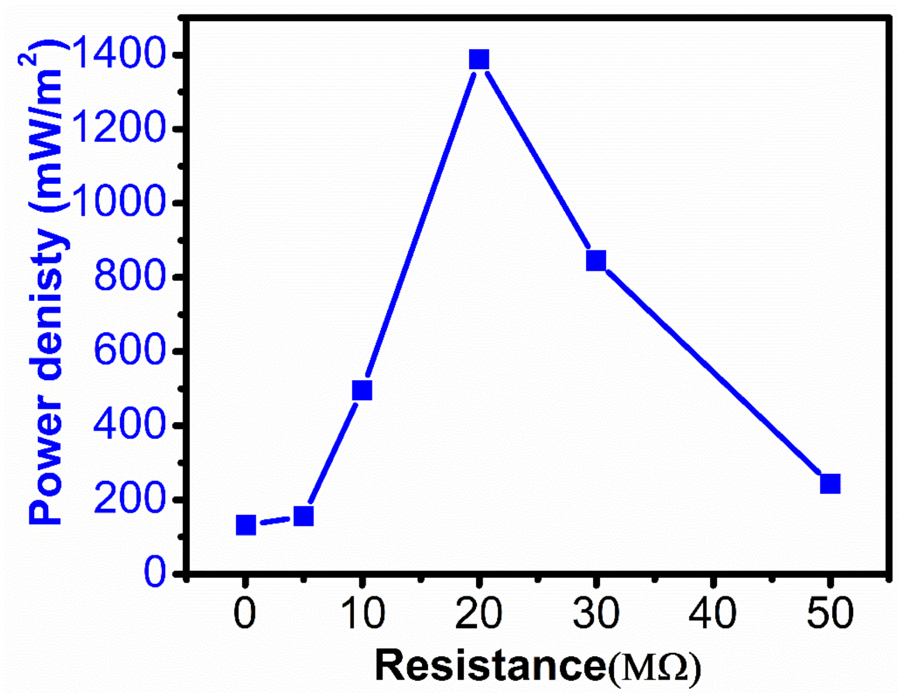

Figure S6 Power density with variable resistance from PDMS−BP NG**.**

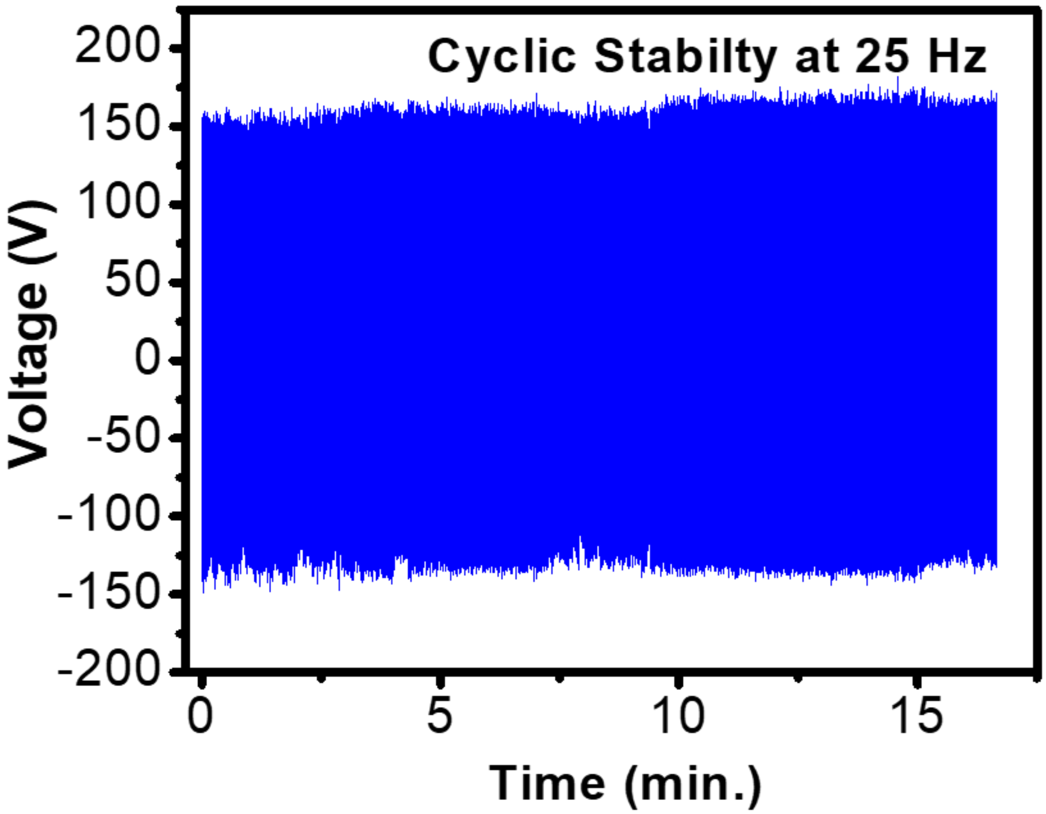

Figure S7 Cyclic stability of Nanogenerator: The peak to peak output voltage of about 200 V was consistently observed for over 30,000 cycles of impact application, confirming the excellent reliability and robustness of PDMS−BP nanosheets device.

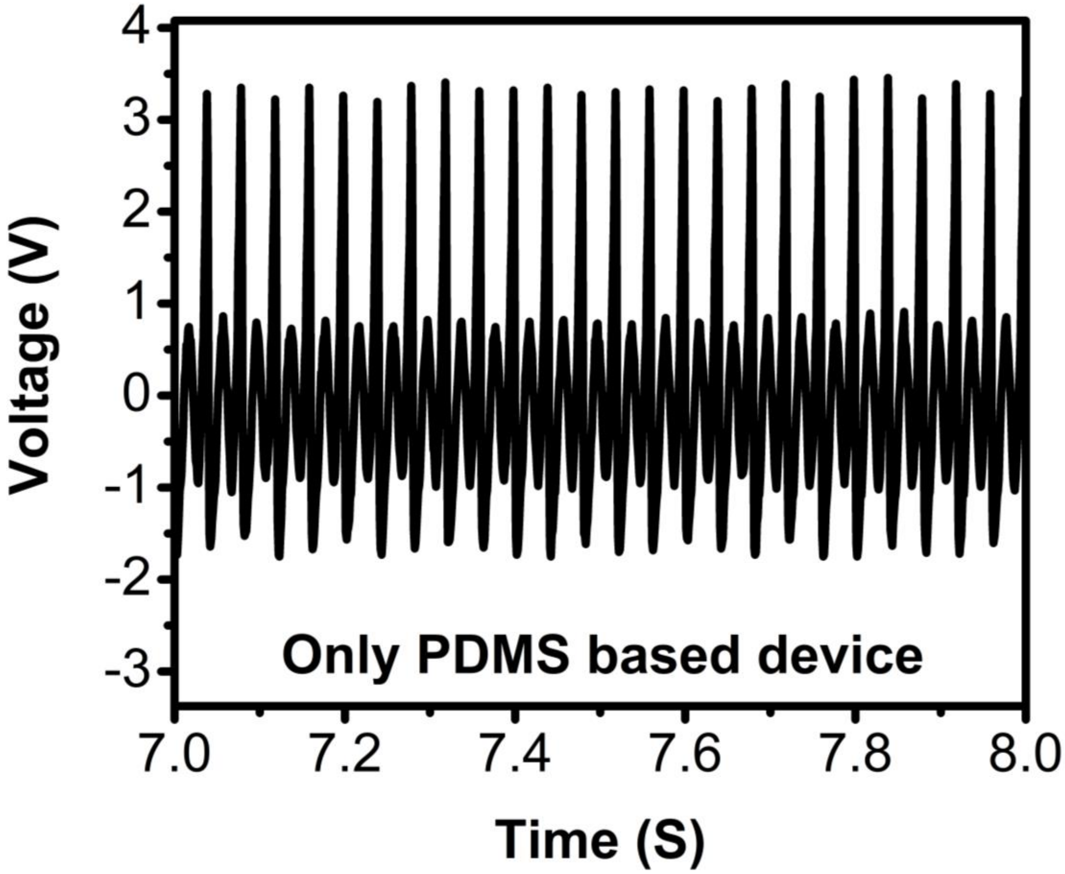

Figure S8 Peak to peak output voltage is around 5 V from only PDMS based NG device (i.e. without BP) which is fabricated in the same configuration as composite**.**

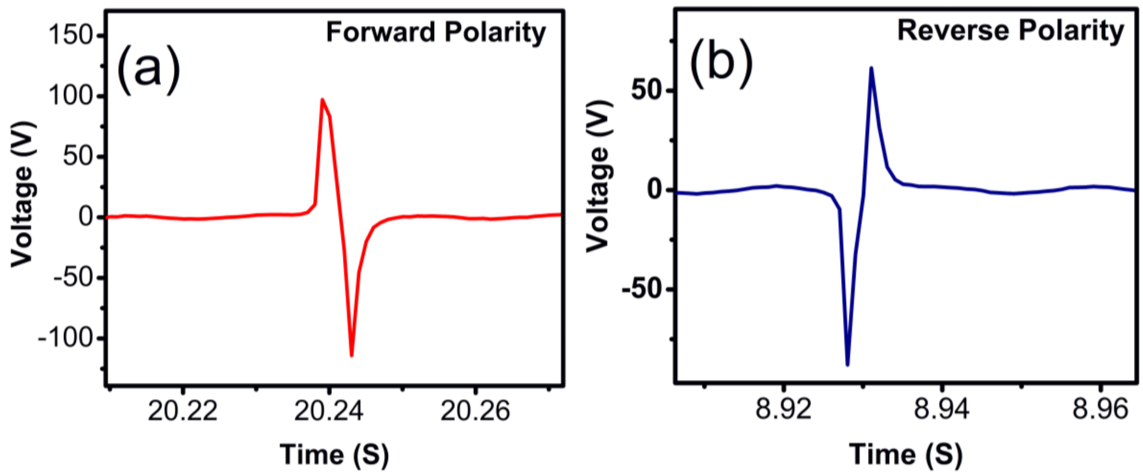

Figure S9 (a) Polarity switchablity Test by Forward connections, **(b)** Voltage signal is reversed by reverse connection which shows polarization switchable behavior of BP-PDMS Nanogenrator**.**

Black phosphorus is a piezo resistive material (Nano Lett.2017, 17, 6097). As we apply mechanical deformation during reverse polarity to the BP-PDMS composite device, we encounter a loss in the output voltage signal. The possible reason for this is resistance change in polymer composite, which drops the total output voltage signal in polarity reversal case. (Transducers'11, Beijing, China, June 5-9, 2011).

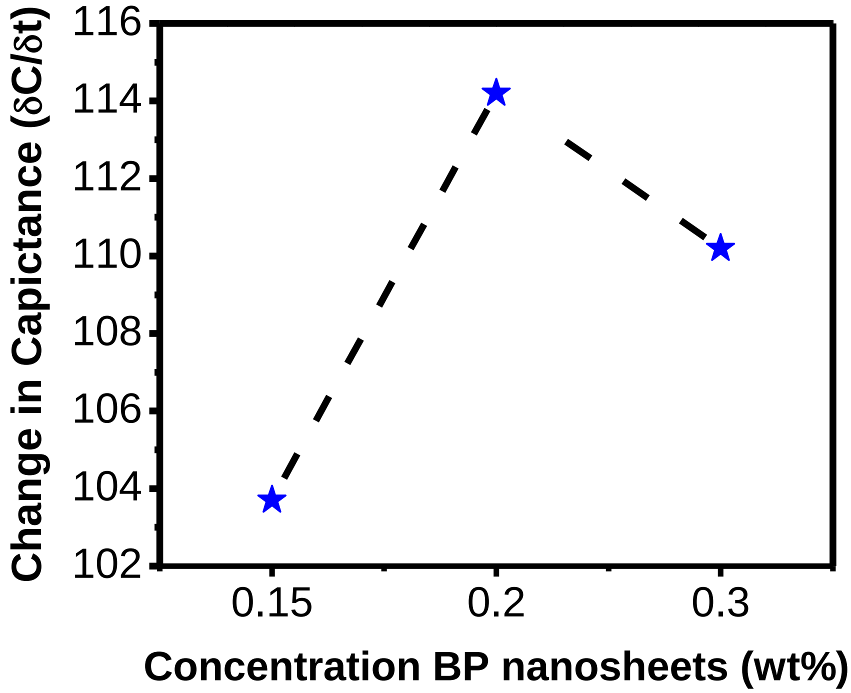

Figure S10 Measurement of change in capictance time gradient with different weight ratio of Black Phosphorus in PDMS **.**

We found that dC/dt in the case of 0.3 weight percentage dropped from the maximum dC/dt (0.2% case).

$$I = dQ/dt = C\ dV/dt + V\ dC/dt$$

Where *I* is short circuit current and *Q* is the stored charges in the capacitor. The second term is imperative for triboelectric effect because it depends on gap between two dielectric materials or triboelectric layers. Figure S10 (SI) shows the variation in capacitance w.r.t time studied for different concentrations of Black Phosphorus in PDMS. We observed highest variation in capacitance in 0.2% (wt%) concentration case. It is resulting the same trend as variation in output voltage with different concentration. *(Ref: Materials today, 20, 74, 2017)*

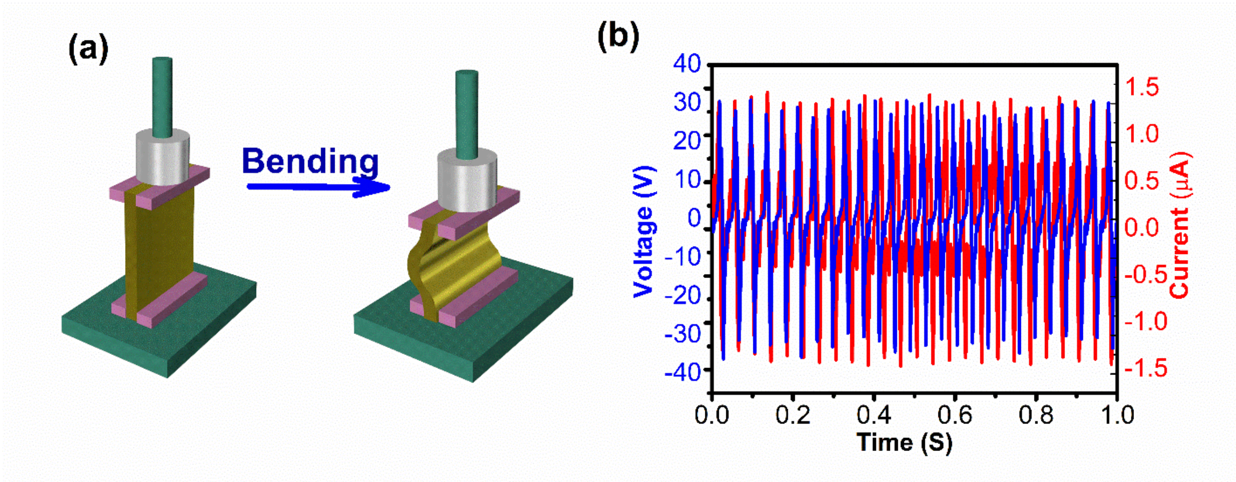

Figure S11 (a) Schematic diagram of relax stage to bending stage of vertical PDMS-BP nanosheets device, (b) open circuit voltage and short circuit current from relax-bending mechanism.

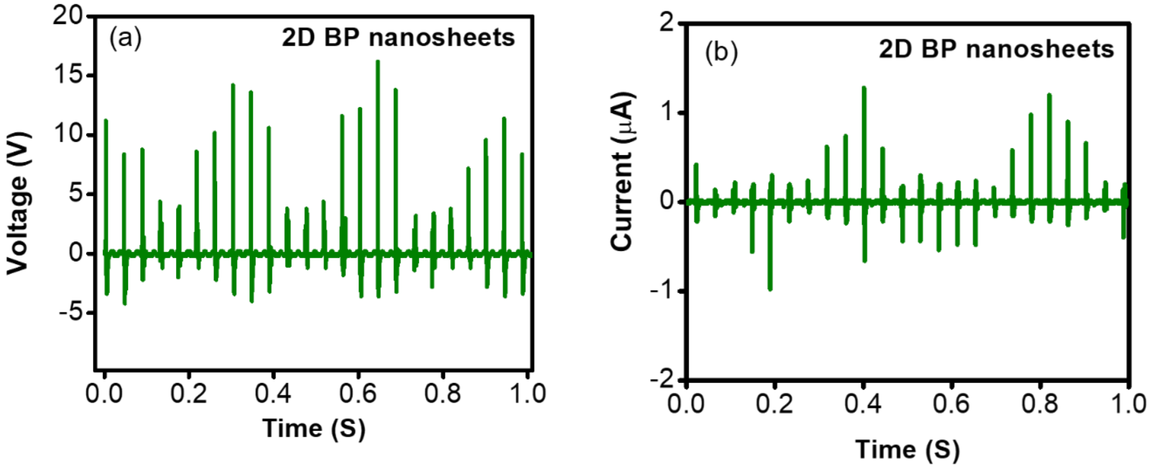

Figure S12 Performance of only BP nanosheets based NG: a) Open circuit voltage, b) Current using 10 MΩ load resistance.

The output performance from only BP nanosheets based nanogenerator showed in Figure S12 shows inconsistent voltage signal because of distribution of nanosheets on substrate was improper as a film. So for the improvement and stabilty of BP nanosheets,we encapsulated BP nanosheets into Polydimethylsiloxane (PDMS)

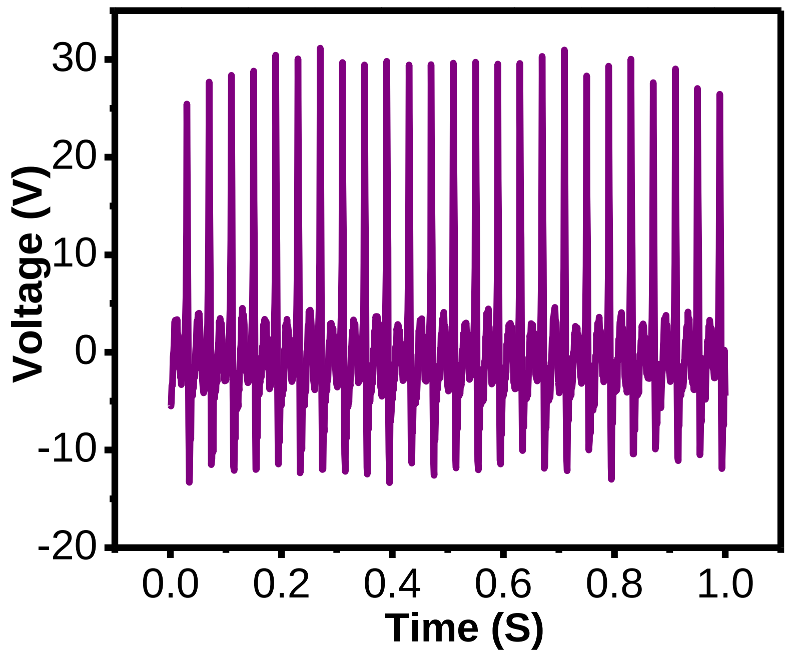

Figure S13 Single electrode measurement to counter the argument about possible triboelectric contribution by friction between electrode and PDMS-BP nanosheets composite film.

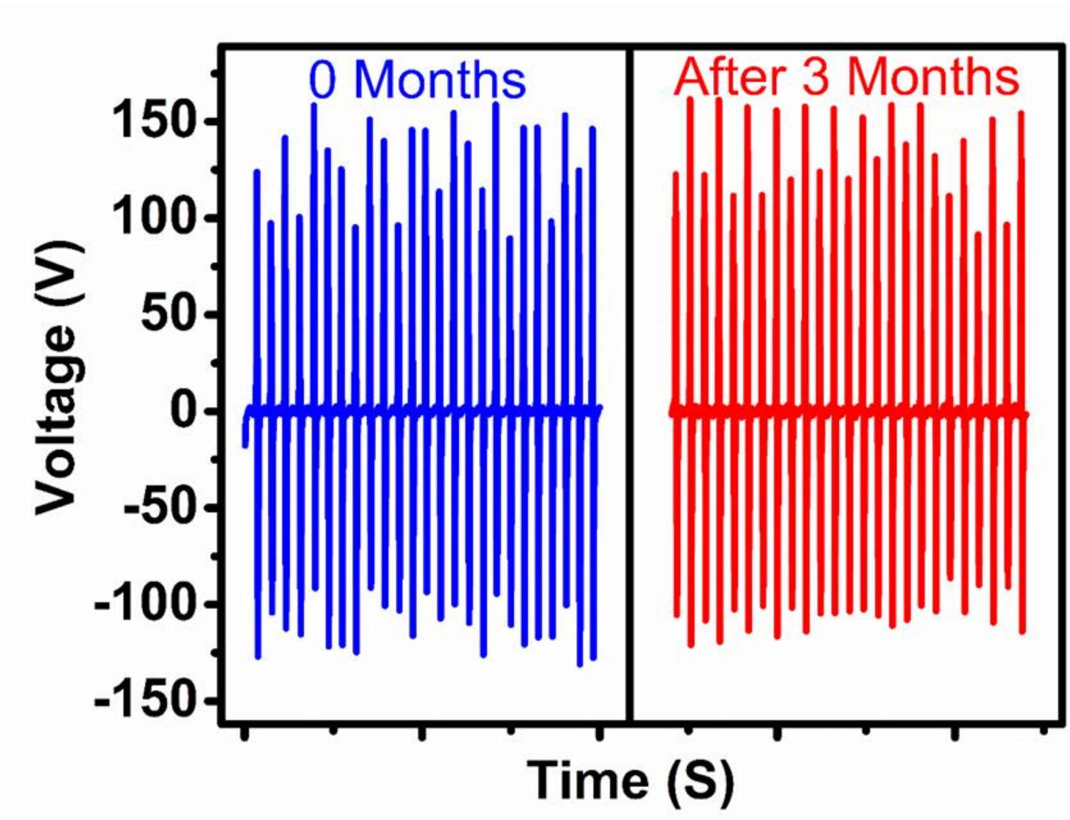

Figure S14 To check the stability of PDMS-BP nanosheets composite based NGs, we tested the output voltage of same device after 3 months; which shows that NG device is completely friendly with the environment, thanks to the PDMS protection of BP.

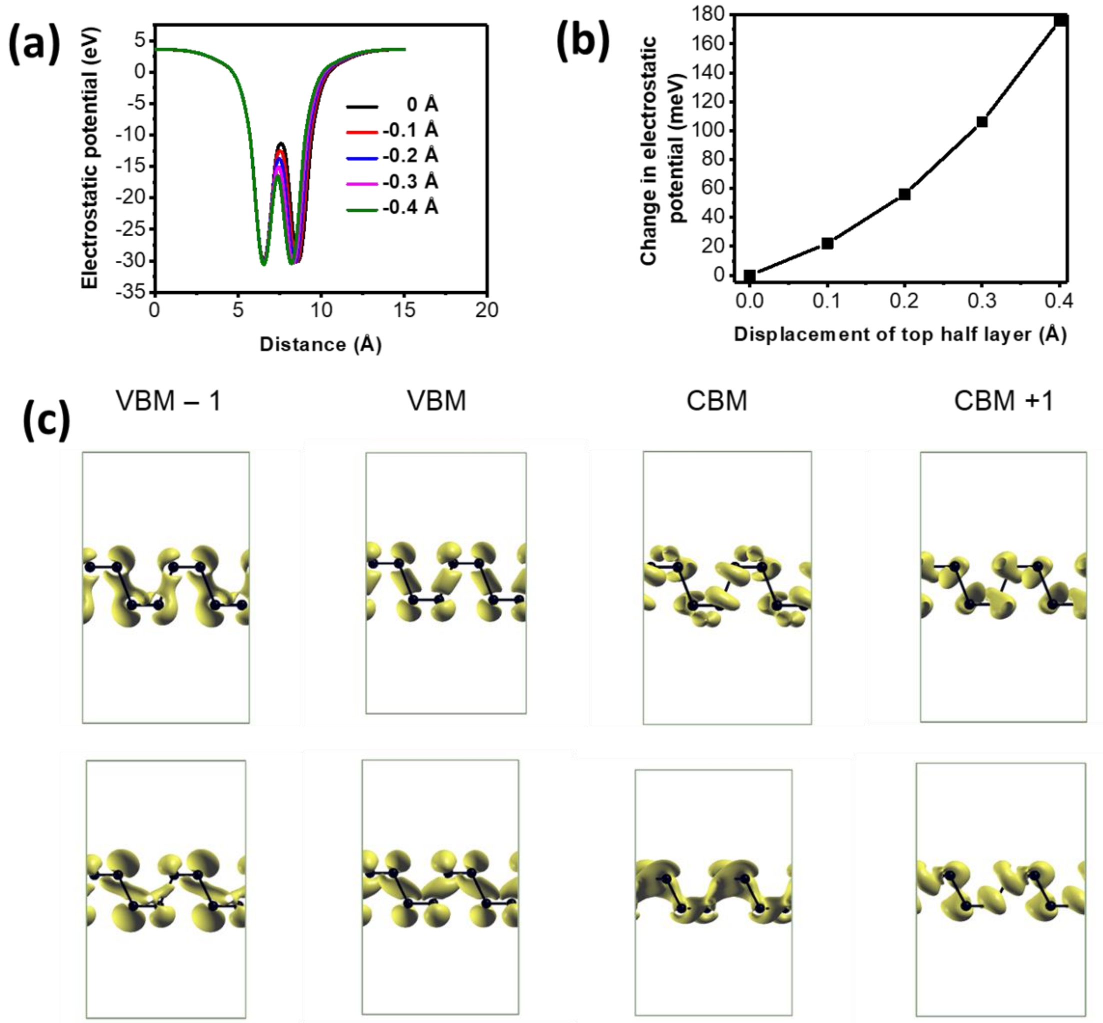

Figure S15 The intralayer electrostatic potential changes with increasing strain. **(**a**)** Calculated plane-averaged electrostatic potential along the direction of strain, **(**b**)** A difference in the potential energy emerges for the two half-layers for an increasing compressive strain and **(**c**)** Interlayer polarization in few-layer black phosphorus**:** Band decomposed charge densities of the low-energy states for the unstrained **(**top row**)** and strained **(**bottom row**)** phosphorene **(**isovalue: 0.01 e/Å^3**).** A charge density gradient develops along the direction of applied force**.** Here, VBM and CBM refer valence band maximum and conduction band minimum**.**

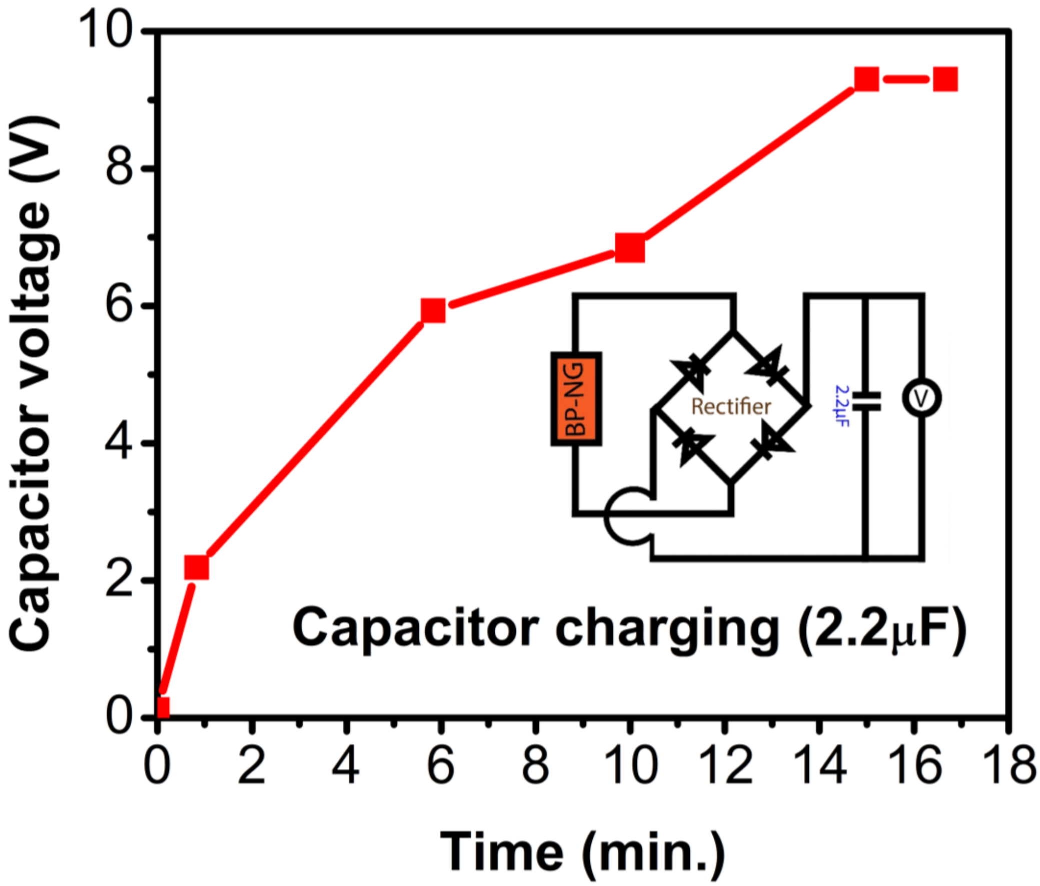

Figure S16 The Power generated from NG stored in 2.2 μF capacitor using a full wave rectifier Voltage across capacitor reached up to 9.30 Volt in 17 minutes.

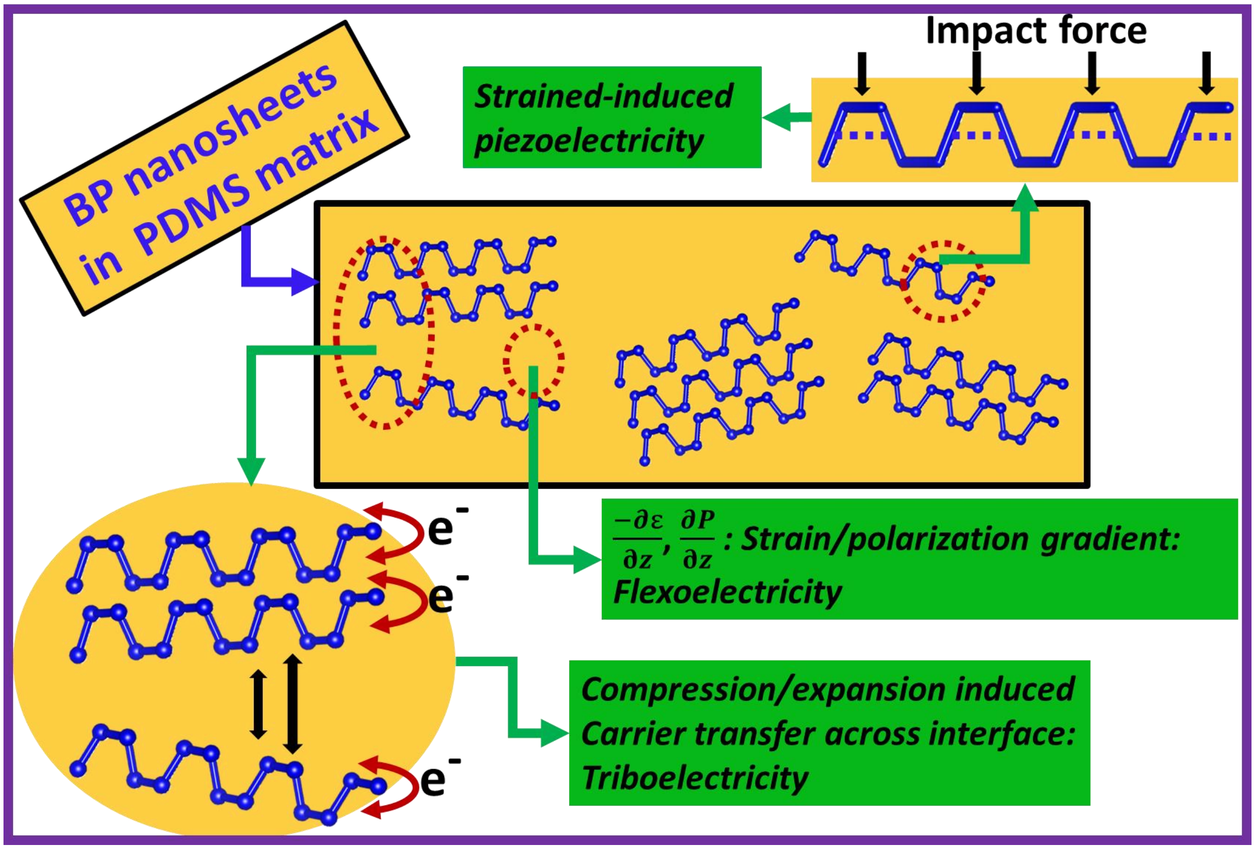

Figure S17 Schematic of multi-mechanism effect proposed by experimental analysis

Table ST1: Comparison of the performance of our device with recently reported black phosphorus-based devices.

Reference	Material/Device	Peak to Peak maximum Voltage (V)	Current Density (mA/m^2)	Power Density (mW/m^2)	Volume Power Density (kW/m^3)	Piezoelectric force microscopy (PFM) study
ACS Energy Lett. 2017, 2, 1797	Electrochemical Device using Sodiated BP	0.013	0.5	0.42	Not Discussed	No
Adv. Mater. Interfaces 2017, 4, 1700651	Cellulose-Phosphorene Hybrid Paper	7.2	0.18	0.11	Not Discussed	No
Adv. Mater. 2018, 30, 1705088	MoS_2/BP Turbotronic gate FET	--	--	--	Not Discussed	No
Our data	**FLBP/PDMS Multi-Mechanism System**	**350**	**12.8**	**1400**	**2**	**Yes**

Note added: After our paper was submitted and was under review, a paper by Xiong et al. appeared in Nat. Commun. 9, 4280 (October 2018) wherein BP encapsulated with hydrophobic cellulose oleoyl ester nanoparticles is shown to yield an output of (250-880 V, 0.48-1.1 mA/cm^2 at about 4 Hz and 5N force) in triboelectric (TENG) mode which is technically distinctly different than our piezoelectric nanogenerator case.