

Electronic Supplementary Information (ESI)

Morphological interference of two different cobalt oxides derived from hydrothermal protocol and a single two-dimensional metal organic framework precursor to stabilize β -phase of PVDF for flexible piezoelectric nanogenerator

Suparna Ojha, Sarbaranjan Paria, Sumanta Kumar Karan, Suman Kumar Si, Anirban Maitra
Amit Kumar Das, Lopamudra Halder, Aswini Bera, Anurima De, Bhanu Bhusan Khatua*
Materials Science Centre, Indian Institute of Technology Kharagpur, Kharagpur-721302,
West Bengal, India

*Corresponding Author

Dr. B.B. Khatua (khatuabb@matsc.iitkgp.ernet.in)

Materials Science Centre, Indian Institute of Technology Kharagpur, Kharagpur-721302

Phone: +91-3222-283982

XRD analysis

The diffraction peaks at $2\theta \sim 19^\circ, 38^\circ, 51.4^\circ, 58.2^\circ$ correspond to the (002), (102), (104), (110) planes of H-Co(OH)_2 which matches with the JCPDS card no-00-002-1094.¹

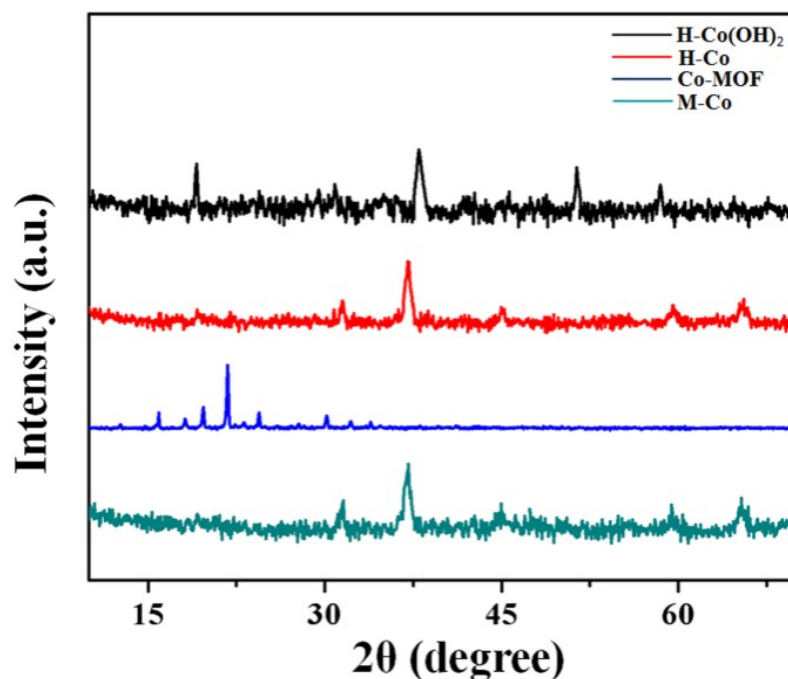


Fig. S1. X-ray diffraction patterns of hydrothermally synthesised Co(OH)_2 , Co-MOF (before annealing) and their corresponding Co_3O_4 .

FT-IR analysis

The appearance of FT-IR peak at 671.48 cm^{-1} for all the three Co_3O_4 is because of the stretching vibrations of Co^{2+} in tetrahedral site. The peak at 580.57 cm^{-1} appears due to vibrations of Co^{3+} in octahedral site and it shows the presence of single-phase face-centered spinel structure Co_3O_4 .²

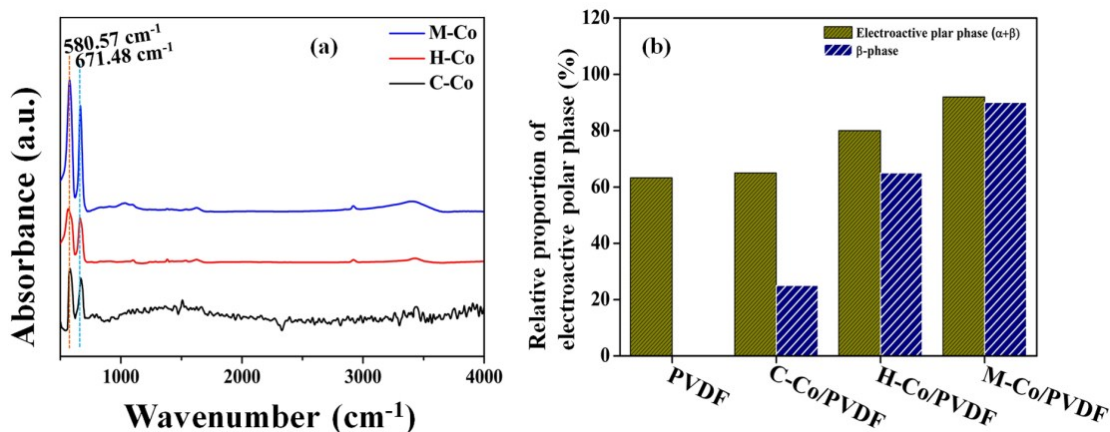


Fig. S2. (a) FT-IR spectroscopy of commercially bought Co_3O_4 , hydrothermally synthesised Co_3O_4 and Metal Organic Framework using synthesised Co_3O_4 . (b) The variation of relative proportion of electroactive polar phase (%) in pure PVDF and three different PVDF nanocomposites.

Calculation of crystallinity

The relative proportion of γ -phase in pure PVDF film was calculated from the equation given below:

$$F(\gamma) = \frac{A_{832}}{A_{832} + A_{764} \left(\frac{K_{832}}{K_{764}} \right)} \times 100\%$$

Where, A_{832} and A_{764} are the absorbance at 832 and 764 cm^{-1} respectively. K_{832} and K_{764} are the absorption coefficients at their respective wave numbers. From the equation, the calculated γ -phase is found to be 63.25% for neat PVDF and α phase is 36.75%.³

Where, A_{832} and A_{764} are the absorption intensities at 832 and 764 cm^{-1} respectively. K_{832} and K_{764} are the absorption coefficients at their respective wave numbers. The relative proportion of polar phases in M-Co/PVDF sample was calculated from the following equation.

$$F(\beta, \gamma) = \frac{A_{841}}{A_{841} + A_{832} \left(\frac{K_{841}}{K_{832}} \right)} \times 100\%$$

$$= 92 \%$$

Where A_{841} is the absorption intensity and K_{841} is absorption coefficient at 841 cm^{-1} respectively. As calculated, the M-Co/PVDF shows the amount of polar phases (β, γ) $\sim 92\%$ at 1.5 wt% M-Co loading out of which $F(\beta) \approx 90\%$ and $F(\gamma) \approx 2\%$ were obtained following the equations, given below:

$$F_{\beta} = F(\beta, \gamma) \times \frac{A_{\beta}}{(A_{\beta} + A_{\gamma})} \times 100\%$$

$$F_{\gamma} = F(\beta, \gamma) \times \frac{A_{\gamma}}{(A_{\beta} + A_{\gamma})} \times 100\%$$

Where A_{β} and A_{γ} are the integrated areas obtained from the deconvolution of the β and γ marked curves as shown in Fig S3.

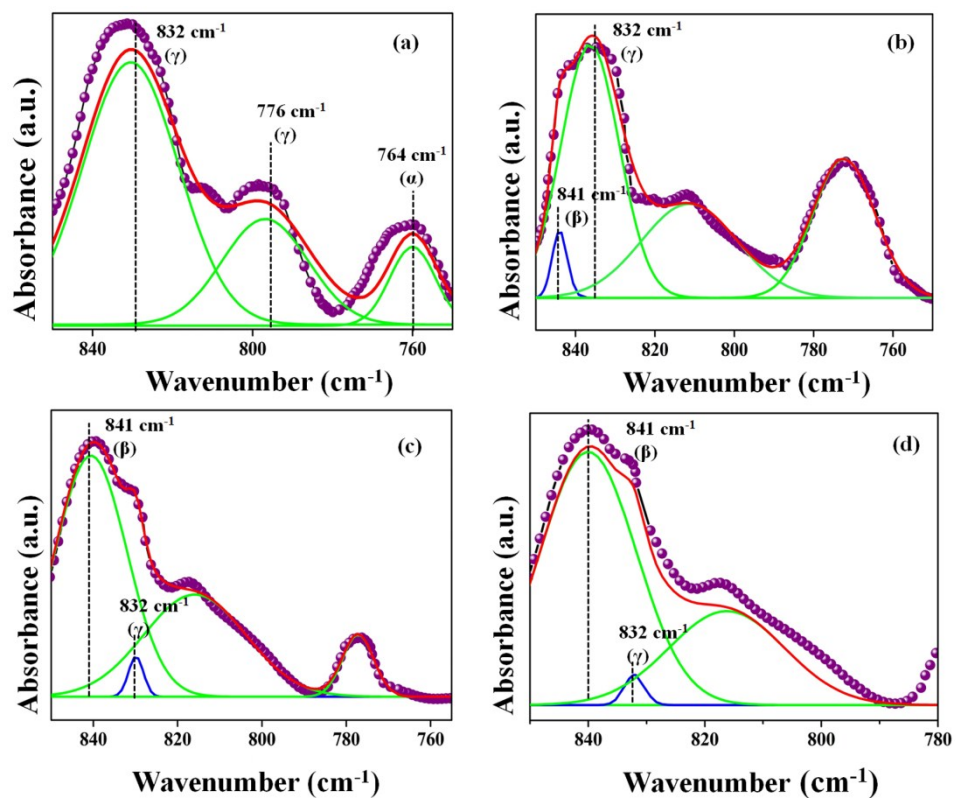


Fig. S3: Deconvoluted FT-IR spectra corresponding to α , β , and γ -phases of (a) pure PVDF, (b) C-Co/PVDF, (c) H-Co/PVDF and (d) M-Co/PVDF nanocomposite.

Zeta potential distribution

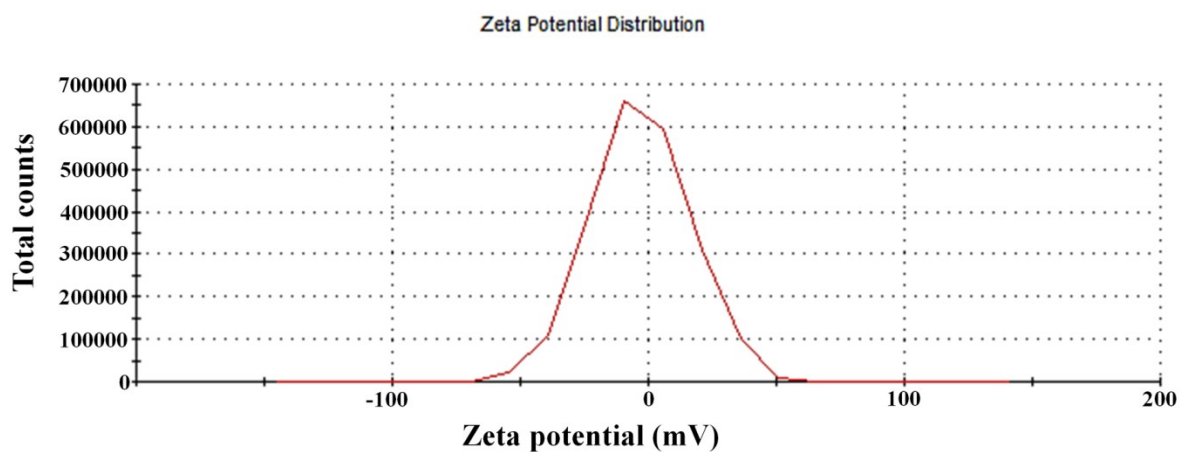


Fig. S4: Zeta potential distribution of M-Co

Morphological analysis

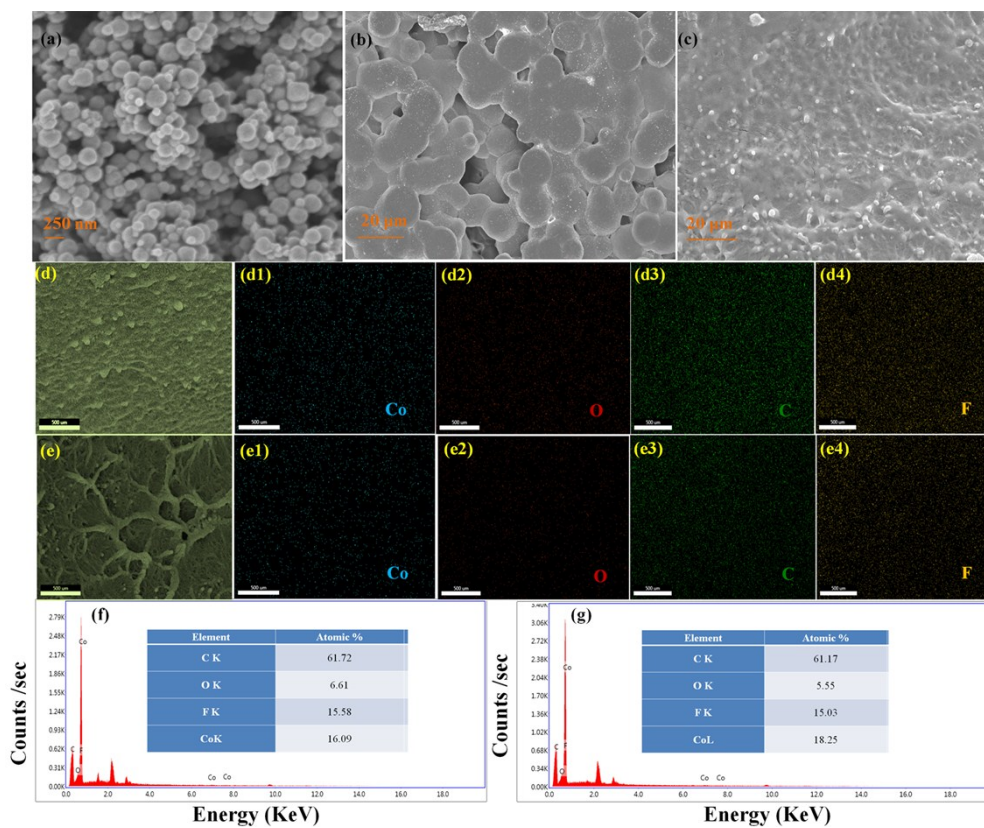


Fig. S5: FESEM image of (a) C-Co nanoparticles, (b) pure PVDF film on 20 μm scale, (c) M-Co/PVDF nanocomposite on 20 μm scale. EDX mapping result of (d) H-Co/PVDF, (e) M-Co/PVDF nanocomposite, and EDX analysis of (f) H-Co/PVDF, (g) M-Co/PVDF nanocomposite.

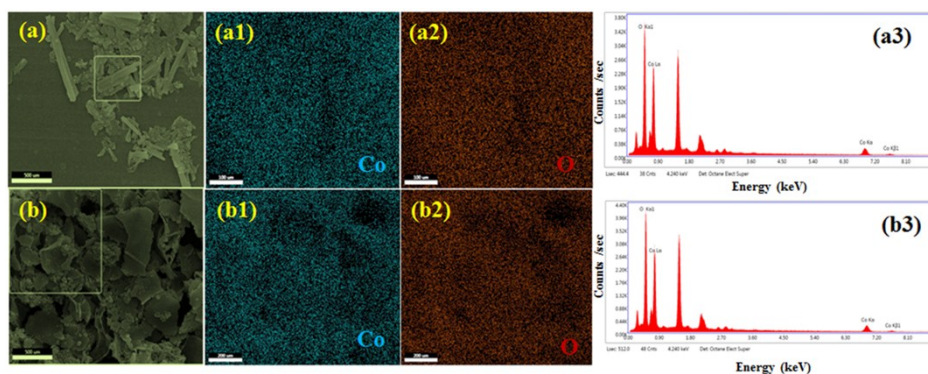


Fig. S6: EDX Mapping result of (a) H-Co, (b) M-Co. EDX analysis of (a3) H-Co and (b3) M-Co.

Specific surface area analysis

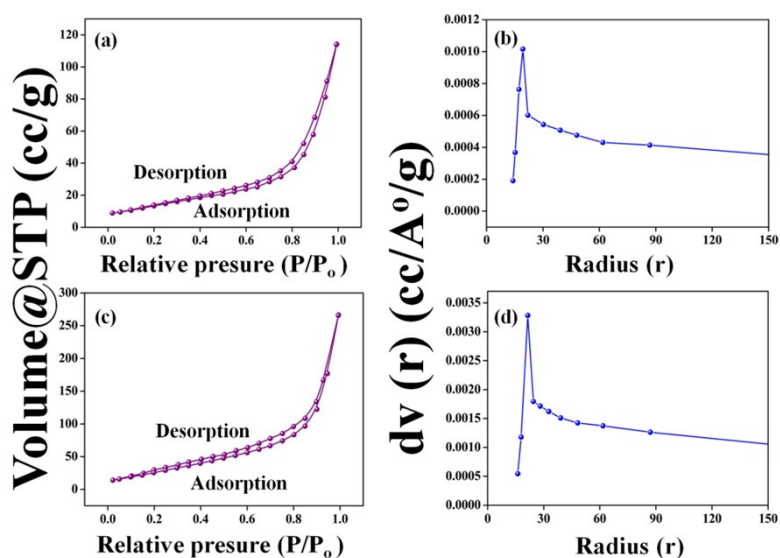


Fig. S7: N₂ adsorption isotherm of (a) H-Co, (c) M-Co and pore size distribution of (b) H-Co, (d) M-Co measured at 77k.

Table S1: The DSC parameters and X_c values of pure PVDF and M-Co/PVDF nanocomposites at various filler loadings.

Filler loading (wt %)	T _m (°C)	T _c (°C)	ΔH _m (J/g)	X _c (%)
0.0	162.7	133.4	38.66	37
0.5	162.3	133.2	39.51	38
1.0	162	133	43.43	41.77
1.5	161.8	132.5	44.03	42.96

Piezoelectric coefficient measurement

Table S2: The obtained piezoelectric coefficient (d_{33}) values of as-prepared nanocomposites.

Nanocomposites	d_{33} value ($\text{pC}\cdot\text{N}^{-1}$)
0.5 M-Co/PVDF	9
1.0 M-Co/PVDF	11
1.5 M-Co/PVDF	16
1.5 H-Co/PVDF	7
1.5 C-Co/PVDF	1

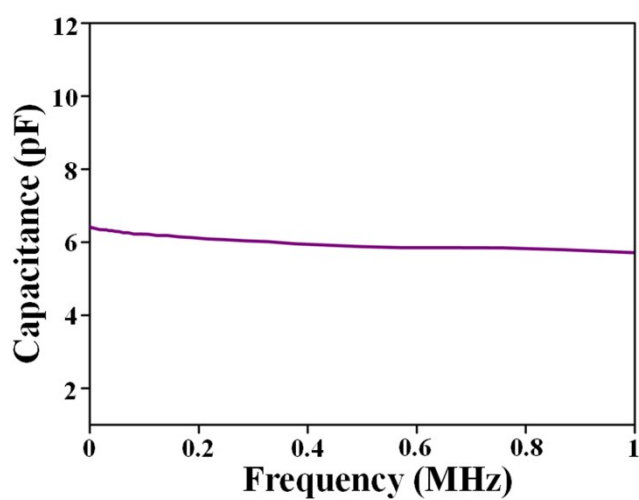


Fig. S8: The variation of capacitance versus frequency curve of 1.5 M-Co/PVDF nanocomposite film, used for MPNG fabrication.

To crosscheck the piezoelectric coefficient values obtained by d_{33} measurement, frequency dependent capacitance measurement was done using impedance analyzer (Agilent 4294A, frequency range of 40 to 3×10^6 Hz), as shown in Fig. S8.

$$V = F \times d_{33} / C$$

where V is the output voltage generated by the MPNG, F is applied force, d_{33} is the piezoelectric coefficient and C is the capacitance, By putting the value ~ 6.6 pF for capacitance, the obtained d_{33} value ~ 16 pC/N⁻¹ for 1.5 M-Co/PVDF nanocomposite, the output voltage generated by the MPNG is found to be ~ 36 V. So from the above discussion it can be concluded that the output voltage obtained from the fabricated MPNG is compatible with the piezoelectric frame of references.

Calculation of operating pressure under human finger imparting condition

The determination of the applied pressure developed by finger impact involving the physical model combining the gravity and pulse term can be done by using following equations:

$$mgh = \frac{1}{2}mv^2$$

$$(F - mg)\Delta t = mv$$

$$\sigma = \frac{F}{S}$$

Where m is mass of the body, h is height of falling, v stands for maximum velocity of falling, σ represents the pressure developed during contact or applied stress, F is the contact force, S is the contact area, Δt is the time spanning during second process. Here $S = 800$ mm² electrode area of the MPNG. $m = \sim 1.1$ kg as measured by using a laboratory balance, $\Delta t =$

0.42 sec is the measured average time variation between the two successive voltage peaks, $h = \sim 0.11$ m and $g = 9.8$ N/kg. So, from the above values the calculated input force, $F \sim 14.8$ N which gives the contact pressure, $\sigma \sim 18.5$ kPa.

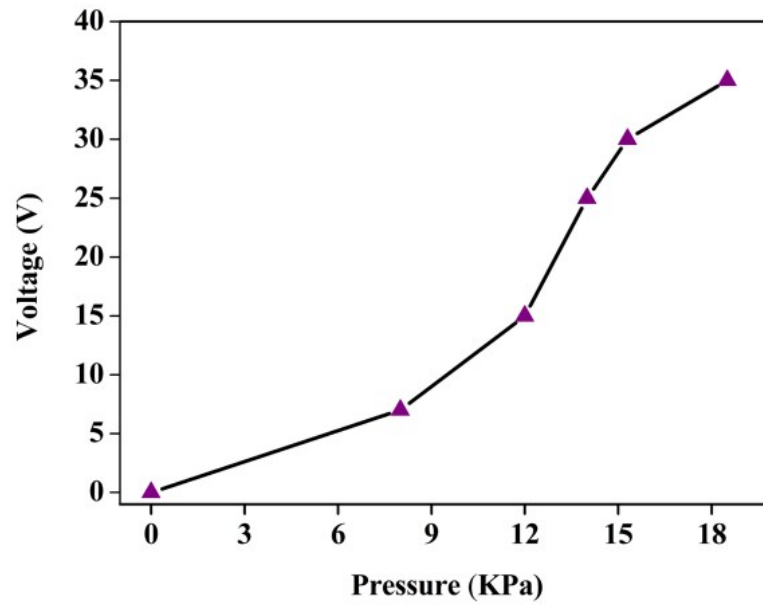


Fig. S9: The variation in the voltage generated from MPNG with the pressure generated by finger imparting

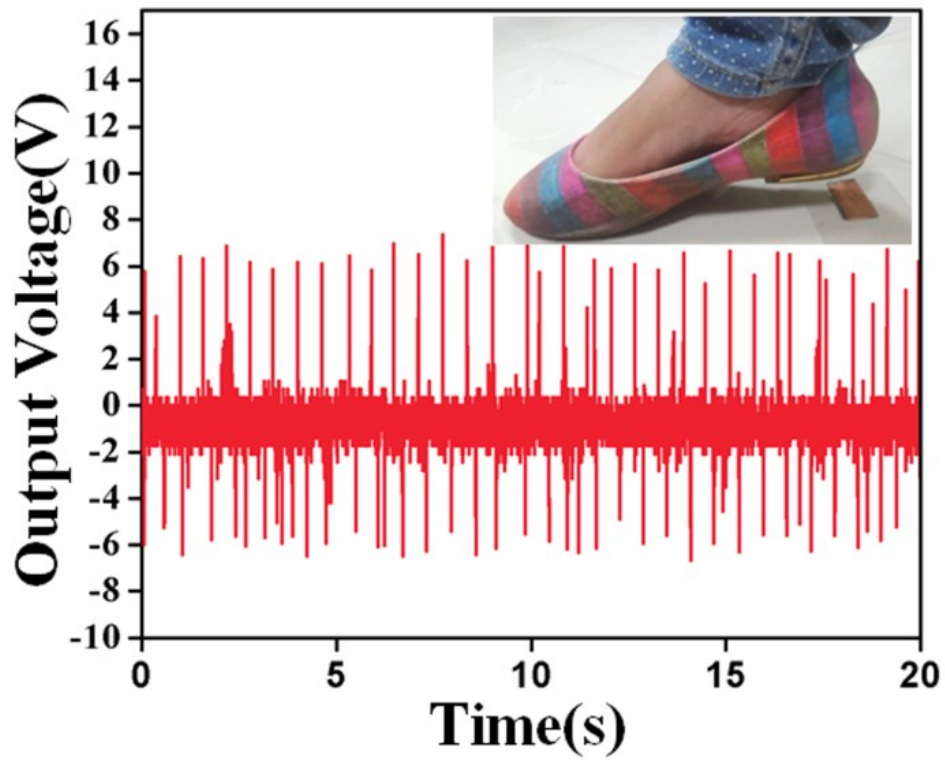


Fig. S10: The generated output voltage from the MPNG under walking



Fig. S11: Powering of a humidity sensor by fabricated MPNG.

Measurement of stress strain behaviour of the as-prepared film

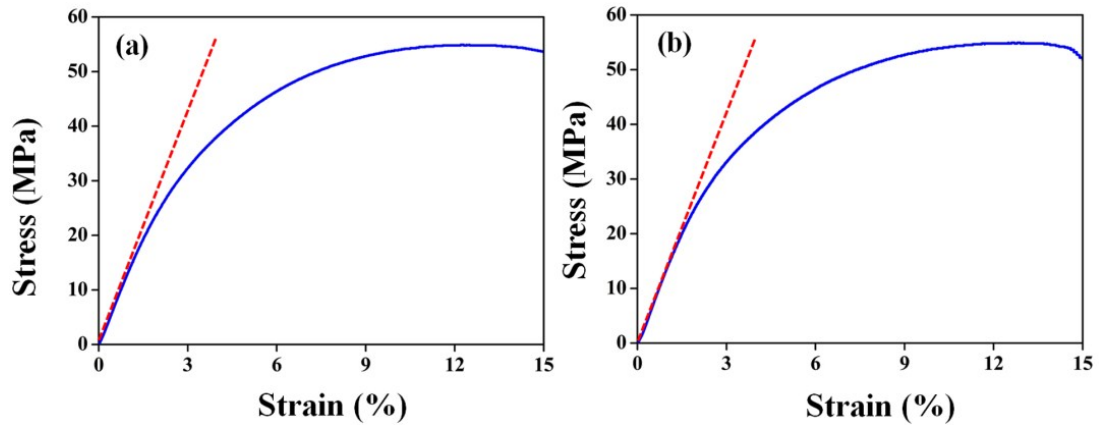


Fig. S12: Stress-strain behaviour of M-Co/PVDF nanocomposite (a) before and (b) after open circuit voltage and short circuit current measurement.

Ferroelectric Properties

The ferroelectric properties of PVDF depends on the presence of electroactive polar phases in the polymer nanocomposites which are responsible for piezoelectric properties. The random orientation of ferroelectric spheres with electric field in PVDF matrix is the main reason behind this piezoelectric behaviour. Among the four distinct crystalline phases, α , β , γ and δ , the β - and γ -phases show ferroelectric properties due to having net dipole moment in their corresponding orientations. The major interest for obtaining electroactive β -phase for ferroelectric properties in which conformation all the H and F atoms are on opposite sides of the backbone chain, i.e. the all trans-conformation which results a non-zero dipole moment.⁴ In PVDF based nanocomposite, the remnant polarization occurs because of the preferred orientation of molecular dipole in the PVDF matrix, which can be obtained by adding suitable filler to the PVDF matrix. After incorporation of M-Co to PVDF matrix, the change in the polarization of the material occurs due to acceleration of internal charge of the nanocomposite as measured by the hysteresis loop. Between voltage signal and charge, energy dissipation of the nanocomposite takes place for which a phase separation is observed. As a result of this, the hysteresis loops are formed with definite area indicating the material having good charge storage capacity. The variation of ferroelectric properties of the M-

Co/PVDF nanocomposites with the electric field (hysteresis loops) is shown in Fig. S13 (a). It is seen that with increasing electric field, the polarization increases and reaches the maxima, suggesting that the orientation of all molecular dipoles contribute to a maximum polarization (with 1.5 wt% M-Co loading). The remnant polarization of the M-Co/PVDF (1.5 wt% M-Co loading) is much greater than those of pure PVDF and its nanocomposite with other M-Co contents (0.5 and 1 wt%) and reaches its highest polarization value of $\sim 1.004 \mu\text{C}/\text{cm}^2$.

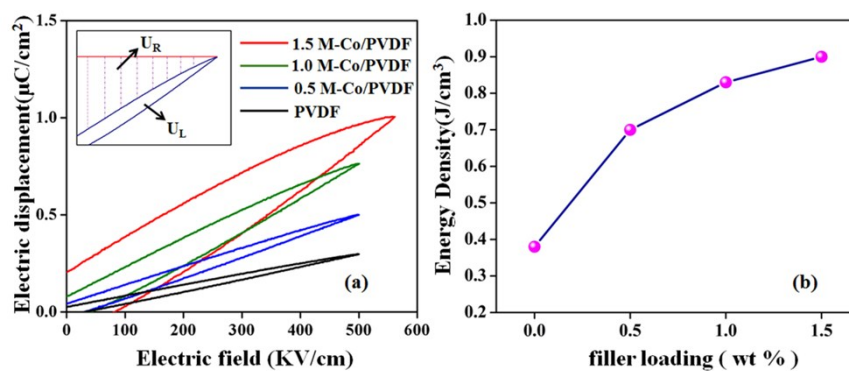


Fig. S13: (a) The P-E loops of pure PVDF and M-Co/PVDF with different Co_3O_4 loadings and in inset represents zone of released energy (U_R) and zone of loss energy (U_L), (b) The variation of released energy density with various filler loadings in the M-Co/PVDF nanocomposites.

Table S3: The calculated values of released and loss energy density, efficiency of the nanocomposite at different filler loadings at an electric field of $537 \text{ kV}/\text{cm}$.

M-Co loading (wt %)	Released energy density (U_R) (J/cm^3)	Energy loss density (U_L) (J/cm^3)	Efficiency ($U_R/(U_R+U_L)$)
0.0	0.38	0.31	0.55
0.5	0.70	0.52	0.57

1.0	0.83	0.57	0.59
1.5	0.90	0.60	0.60

As the energy storage capacity of the nanocomposite is higher, so it is excellent for piezoelectric applications. In the inset it is shown that by integrating the labelled outside area the released energy density (U_R) has been calculated. By integrating the area inside the hysteresis loop, the energy loss (U_L) can be obtained. And the total energy (U_T) stored inside the nanocomposite can be calculated from the summation of the U_R and U_L . The efficiency of the nanocomposite can be calculated from the ratio between U_R and U_T , as shown in Table 3 (ESI). Fig. S13 (b) shows the released energy density (E_R) of the nanocomposites with different M-Co loadings. The released energy density (U_R) of 1.5% M-Co /PVDF nanocomposite is 0.90 J cm^{-3} , that is much higher than the pure PVDF (0.38 J cm^{-3}).⁵

Also a suitable filler helps in interfacial polarization of material which occurs at the inner partitions of conductive heterogeneous material. In this case filler acts as more conducting in nature than polymer matrix mobilization through the particles and accelerate the hetero polarization of the material.

SV 1: Lightening of LEDs in parallel connection, series connection, capacitor charging, powering up speaker, wrist watch.

SV 2: Powering up humidity sensor, calculator.

References

1. T. Xu, G. Li and L. Zhao, *Chem. Eng. J.*, 2018, **336**, 602-611.
2. C. Anuradha and P. Raji, *Int. J. Nanosci.*, 2019, 1950002.
3. S. K. Karan, R. Bera, S. Paria, A. K. Das, S. Maiti, A. Maitra and B. B. Khatua, *Adv. Energy Mater.*, 2016, **6**, 1601016.
4. M. Sharma, G. Madras and S. Bose, *Phys. Chem. Chem. Phys.*, 2014, **16**, 14792-14799.
5. S. K. Karan, D. Mandal and B. B. Khatua, *Nanoscale*, 2015, **7**, 10655-10666.