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

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XRD analysis

The diffraction peaks at 2θ ~19°, 38°, 51.4°, 58.2° correspond to the (002), (102), (104), (110) planes of H-Co(OH)$_2$ which matches with the JCPDS card no-00-002-1094.$^1$

![X-ray diffraction patterns](image)

**Fig. S1.** X-ray diffraction patterns of hydrothermally synthesised Co(OH)$_2$, Co-MOF (before annealing) and their corresponding Co$_3$O$_4$.

FT-IR analysis

The appearance of FT-IR peak at 671.48 cm$^{-1}$ for all the three Co$_3$O$_4$ 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$_3$O$_4$.$^2$
Fig. S2. (a) FT-IR spectroscopy of commercially bought Co$_3$O$_4$, hydrothermally synthesised Co$_3$O$_4$ and Metal Organic Framework using synthesised Co$_3$O$_4$. (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:

\[
F(\gamma) = \frac{A_{832}}{A_{832} + A_{764}} \times \frac{K_{832}}{K_{764}} \times 100\% 
\]

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%.

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 ($\beta$, $\gamma$) $\sim 92\%$ 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 $A_\beta$ and $A_\gamma$ are the integrated areas obtained from the deconvolution of the $\beta$ and $\gamma$ marked curves as shown in Fig S3.
**Fig. S3:** Deconvoluted FT-IR spectra corresponding to $\alpha$, $\beta$, and $\gamma$-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**

![Graphs showing nitrogen adsorption isotherm and pore size distribution](image_url)

**Fig. S7:** N$_2$ 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.

<table>
<thead>
<tr>
<th>Filler loading (wt %)</th>
<th>$T_m$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>162.7</td>
<td>133.4</td>
<td>38.66</td>
<td>37</td>
</tr>
<tr>
<td>0.5</td>
<td>162.3</td>
<td>133.2</td>
<td>39.51</td>
<td>38</td>
</tr>
<tr>
<td>1.0</td>
<td>162</td>
<td>133</td>
<td>43.43</td>
<td>41.77</td>
</tr>
<tr>
<td>1.5</td>
<td>161.8</td>
<td>132.5</td>
<td>44.03</td>
<td>42.96</td>
</tr>
</tbody>
</table>
Piezoelectric coefficient measurement

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

<table>
<thead>
<tr>
<th>Nanocomposites</th>
<th>$d_{33}$ value (pCN$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 M-Co/PVDF</td>
<td>9</td>
</tr>
<tr>
<td>1.0 M-Co/PVDF</td>
<td>11</td>
</tr>
<tr>
<td>1.5 M-Co/PVDF</td>
<td>16</td>
</tr>
<tr>
<td>1.5 H-Co/PVDF</td>
<td>7</td>
</tr>
<tr>
<td>1.5 C-Co/PVDF</td>
<td>1</td>
</tr>
</tbody>
</table>

**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 \( 3 \times 10^6 \) 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 \( \sim 6.6 \) pF for capacitance, the obtained \( d_{33} \) value \( \sim 16 \) pCN\(^{-1}\) for 1.5 M-Co/PVDF nanocomposite, the output voltage generated by the MPNG is found to be \( \sim 36 \) 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, \( \sigma \) represents the pressure developed during contact or applied stress, \( F \) is the contact force, \( S \) is the contact area, \( \Delta t \) is the time spanning during second process. Here \( S = 800 \) mm\(^2\) 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, \( h \approx 0.11 \text{ m} \) and \( g = 9.8 \text{ N/kg} \). So, from the above values the calculated input force, \( F \approx 14.8 \text{ N} \) which gives the contact pressure, \( \sigma \approx 18.5 \text{ kPa} \).

**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, $\alpha$, $\beta$, $\gamma$ and $\delta$, the $\beta$- and $\gamma$-phases show ferroelectric properties due to having net dipole moment in their corresponding orientations. The major interest for obtaining electroactive $\beta$-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. 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 \(~1.004\) \(\mu\)C/cm\(^2\).

**Fig. S13:** (a) The P-E loops of pure PVDF and M-Co/PVDF with different Co\(_3\)O\(_4\) 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 kV/cm.

<table>
<thead>
<tr>
<th>M-Co loading (wt %)</th>
<th>Released energy density ((U_R)) (J/cm(^3))</th>
<th>Energy loss density ((U_L)) (J/cm(^3))</th>
<th>Efficiency ((U_R/(U_R+U_L)))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.38</td>
<td>0.31</td>
<td>0.55</td>
</tr>
<tr>
<td>0.5</td>
<td>0.70</td>
<td>0.52</td>
<td>0.57</td>
</tr>
</tbody>
</table>
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$^{-3}$)\textsuperscript{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

2. C. Anuradha and P. Raji, *Int. J. Nanosci.*, 2019, **1950002**.