Electronic Supplementary Information (ESI)

Title: Enhanced dielectric, ferroelectric, energy storage and mechanical energy harvesting performance of ZnO-PVDF composites induced by MWCNT as an additive third phase

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Fig. S1 (a) Frequency dependent dielectric permittivity and dielectric loss, (b) Polarization vs applied electric field (D-E) loop, (c) Comparison of open circuit output a.c. voltage of 15PZO-0 wt% CNT, 15PZO-0.05 wt%, 15PZO-0.1 wt% CNT and 15PZO-0.15 wt% CNT composite films.

Optimization of concentration of MWCNT

For optimization the MWCNT concentration in PVDF-ZnO matrix, composite films were fabricated by adding 15 wt% ZnO and different amount MWCNT (0, 0.05 wt%, 0.1 wt% and 0.15 wt%, respectively, for 15PZO-0 wt% CNT, 15PZO-0.05 wt% CNT, 15PZO-0.1 wt% CNT and 15PZO-0.2 wt% CNT) in PVDF matrix. Electrical performance of the composite films enhanced with increasing MWCNT concentration up to 0.1 wt% which was considered to be due to the formation of conductive network; but, further addition of MWCNT beyond

0.1 wt% caused the reduction in electrical performance which might be due to the increased agglomeration of MWCNT in the composite system. Though the dielectric permittivity increased gradually with 0.05, 0.1 and 0.15 wt% MWCNT addition in 15PZO film, the dielectric loss also increased significantly beyond 0.1 wt% which was due to the formation of more MWCNT agglomeration (Fig. S1(a)). The 15PZO-0.15 wt% CNT composites exhibited maximum value of dielectric permittivity but its dielectric loss tangent was very high. Therefore, this system was excluded. Hence, the 15PZO-0.1 wt% CNT film, exhibiting low dielectric loss along with significantly high dielectric permittivity, was chosen as the optimized one. The highly lossy nature of 15PZO-0.15 wt% CNT film was also confirmed from the study of P-E hysteresis loops of all the films (Fig. S1(b)). This lossy nature will result into the reduction of energy storage performance. Output voltage was also found to be maximum for 15PZO-0.1 wt% CNT composite film in comparison to those of other composite films (Fig. S1(c)). Considering all these facts, 15PZO-0.1wt% CNTs was considered as an optimized sample to achieve high electrical performance. Therefore, 0.1 wt% MWCNT loading in the ZnO-PVDF composite films was selected in the present work.

Fig. S2



Fig. S2 (a) Raman spectra and (b) TEM image of MWCNT.

Characterization of MWCNT

Fig .S2 (a) shows the Raman spectrum of CNT. Two strong bands appeared at 1358 cm⁻¹ (D band) and 1582 cm⁻¹ (G band) in raman spectrum. The 'D band' at 1358 cm⁻¹ mainly appeared due to the structural defect in the CNT structure. The 'G band' appeared due to the raman active E_{2g} mode. Fig S2 (b) presents the TEM images of CNT which indicates that average diameter of CNT is ~15 nm.

<u>Fig. S3</u>



Fig S3 (a) Diameter distribution, (b) HRTEM image and (c) EDX spectrum of ZnO nanorods.





Fig. S4 XRD pattern of pure PVDF, 15PZO and 15PZNT composites with 2θ ranging from 10° to 30°.

Crystallinity of the composite films

Total degree of crystallinity and individual amount of beta crystallinity and gamma crystallinity of all composites were calculated from deconvoluted XRD pattern (Fig. 3). The total degree of crystallinity (χ_{c_t}) of the nanocomposites was calculated from Equation E1.

$$\chi_{c_t} = \frac{\Sigma_{A_{cr}}}{\Sigma_{A_{cr}} + \Sigma_{A_{amr}}} \times 100 \%$$
(E1)

where, $\sum A_{cr}$ and $\sum A_{amr}$ are the integral area of crystalline and amorphous region, respectively. Individual amount of beta crystallinity ($\chi_{c_{\beta}}$) and gamma crystallinity ($\chi_{c_{\gamma}}$) were calculated from deconvoluted XRD graph (Fig. 3) from Equation E2 and E3, respectively.

$$\chi_{c_{\beta}} = \chi_{c_{t}} \times \frac{\Sigma_{A_{\beta}}}{\Sigma_{A_{\beta}} + \Sigma_{A_{\gamma}}} \%$$
(E2)

$$\chi_{c_{\gamma}} = \chi_{c_t} \times \frac{\sum_{A_{\gamma}}}{\sum_{A_{\beta}} + \sum_{A_{\gamma}}} \%$$
(E3)

where, $\sum\!A_\beta$ and $\sum\!A_\gamma$ are the total integral area of β peak and γ peak respectively.

The individual quantification of total crystallinity, beta phase crystallinity and gamma phase crystallinity of PVDF, 15PZO and 15PZNT are represented in Table S1.

Table S1

Table S1 Amount of χ_{c_t} , χ_{c_β} and χ_{c_γ} for PVDF, 15PZO and 15PZNT composite films.

Sample Name	Total degree of crystallinity (χ_{c_t}) (%)	Beta phase crystallinity $(\chi_{c_{\beta}})$ (%)	Gama phase crystallinity ($\chi_{c_{\gamma}}$) (%)
PVDF	67.2		
15PZO	56.1	26.55	29.54
15PZNT	32.4	30.6	1.78

<u>Fig. S5</u>



Fig. S5 The deconvoluted FTIR spectra (range within 850-820 cm⁻¹) of PVDF, 15PZO and 15PZNT composites.

Calculation of phase formation in PVDF

The deconvoluted peaks corresponding to β and γ are indicated in the Fig. S5. The Equation E4 and E5 were used to evaluate the individual amount of β and γ phases, respectively.

$$F(\beta) = F_{EA} \times \frac{A_{\beta}}{A_{\beta} + A_{\gamma}} \times 100\%$$
(E4)

$$F(\gamma) = F_{EA} \times \frac{A_{\gamma}}{A_{\beta} + A_{\gamma}} \times 100\%$$
(E5)

where A_{β} and A_{γ} are the integrated area of β peak and γ peak of the deconvoluted curve, respectively. The individual quantification of F(β) and F(γ) from FTIR study for each sample was calculated and shown in Table S2. Relative amount of β phase (w.r.t γ phase) (F_{$\beta\gamma$}) and γ phase (w.r.t to β phase) were also calculated using Equation E6 and E7, respectively.

$$F_{\beta\gamma} = \frac{F(\beta)}{F(\beta) + F(\gamma)} \times 100\%$$
(6)

$$F_{\gamma\beta} = \frac{F(\gamma)}{F(\beta) + F(\gamma)} \times 100\%$$
(7)

Table S2: Individual amount of polar phase calculation for PVDF, 15PZO and 15PZNT composites

Sample Name	Polar phase	B phase	γ phase	Relative	Relative
	Fraction	Fraction	Fraction	amount of β	amount of γ
	(F_{EA}) (%)	$(F_{\beta})(\%)$	(F_{γ}) (%)	phase w.r.t	phase w.r.t
				to γ phase	to β phase
				$(F_{\beta\gamma})$ (%)	$(F_{\gamma\beta})$ (%)
PVDF	43.2	19	24.06	44.1	55.8
PVDF/ZnO	68.5	34.05	34.44	49.7	50.28
PVDF/ZnO/CNT	88.9	45.33	43.56	50.9	49

Damping coefficient

For better interpretation of the interfacial interaction, FTIR spectra of PVDF, 15PZO and 15PZNT samples within the wavenumber region 3100 cm⁻¹ to 2900 cm⁻¹ were studied; because, this region is mainly attributed to symmetric (v_s) and asymmetric (v_{as}) stretching vibration band of -CH₂ dipole which are not coupled with any other vibrational modes. Therefore the absorption spectra within this region provide detailed information about the interfacial interaction between -CH2 dipole of PVDF and nanofiller surface. After incorporation of ZnO filler in PVDF matrix, symmetric and asymmetric stretching vibrational band of -CH₂ dipole shifted towards lower wavenumber region compared to pure PVDF. The gradual shift of vibrational bands towards lower energy can be explained by damped harmonic oscillator model. At first, it was assumed that, these two vibration bands have no damping when no filler was included in PVDF matrix. With filler loading in PVDF matrix damping appeared due to electrostatic interaction between of -CH₂ dipole of PVDF and filler surface. The shifting of these absorption bands towards lower wavenumber region for 15PZNT compared to that of 15PZO film confirmed our earlier assumption of more interfacial electrostatic interaction of -CH₂ dipoles of PVDF with third MWCNT phase. In order to get the quantitative amount of electrostatic interaction, damping coefficient of the composite films was calculated from the peak shifting of the asymmetric -CH₂ stretching vibrational band using Equation E8.

$$r_{dc} = 4\pi C (\bar{\upsilon}_{PVDF}^2 - \bar{\upsilon}_{COMP}^2)^{1/2}$$
(E8)

where r_{dc} represents damping coefficient, C indicates the velocity of light in free space, \bar{v}_{PVDF} and \bar{v}_{COMP} represent the peak position of asymmetric –CH₂ stretching vibrational band of pure PVDF and composites, respectively. The damping coefficients were found to be 0, 3.90×10^{13} and 4.53×10^{13} sec⁻¹, respectively, for neat PVDF, 15PZO and 15PZNT films. The gradual increase in damping coefficient justified our consideration of gradual improvement of interfacial interaction for the respective films.

Fig. S6



Fig. S6 Zeta potential study of ZnO nanorods. The negative value of zeta potential (-20.7 mV) suggested the negative surface charge of the synthesized ZnO nanorods.

Discussion S6

Simulation Parameter

Electric field and polarization were simulated as a function of applied external voltage. Piezoelectric potential was simulated under similar amount of pressure applied on each of the devices for the same dimensions as our fabricated devices. It is well reported that, when rod-shaped fillers are included into PVDF based films, the rods are generally oriented in the inplane direction; i.e., maximum number of rods orient themselves along the plane of the composite film and the occurrence of rod-shaped fillers along the film's thickness is very rare.⁷⁰ But, during simulation, we need to consider the cross section of the composite films. For the sake of simplicity, both the ZnO nanorods and CNTs are considered to be oriented along the length of the film so that the film's cross section contains the cross sections of ZnO nanorods/ CNTs /PVDF matrix. The cross section of ZnO rods were considered as circular as the top surfaces of ZnO nanorods were almost round. Therefore, during simulation, ZnO rods and CNT are represented by big and small circle respectively. The remaining region is filled by PVDF matrix. In our work, a small portion of the film's cross section was considered for simulation for better view. Here, simulation was performed for PVDF/ZnO and PVDF/ZnO/CNT composites to understand the effect of MWCNT addition as a third phase conductive filler in PVDF matrix.

<u>Fig. S7</u>



Fig. S7 Simulated electric field intensity as a function of applied voltage of PVDF/ZnO and PVDF/ZnO/MWCNT composites.





Fig. S8 Simulated polarization distribution as a function of applied voltage of PVDF/ZnO and PVDF/ZnO/MWCNT composites.