

Article

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Energy Harvester and Tactile e-skin Mechanosensor**

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NiO@SiO₂/PVDF: A Flexible Polymer Nanocomposite for High Performance Human Body Motion Based Energy Harvester and Tactile e-skin Mechanosensor

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Abstract

Advancement in self-powered portable and wearable electronics mostly depends on realization of efficient human activity based energy harvester and electronic skin (e-skin) mimicking tactile mechanosensing property of the natural human skin. Human activity based energy harvester can supply power to flexible, potable electronics equipment associated to human body whereas tactile e-skin mechanosensor can precisely detect static and dynamic pressure stimuli. Here we report development of NiO@SiO₂/PVDF nanocomposite, a facile piezoelectric material possessing superior flexibility, light weight and low cost but an excellent choice for next generation mechanical energy harvester and tactile e-skin sensors. The fabricated piezoelectric nanogenerator (PNG) comprising the nanocomposite shows very promising output under application of biomechanical force on it. PNG15 exhibits high output voltage (53 V), adequate current density ($\sim 0.3 \mu\text{A}/\text{cm}^2$), high power density ($685 \text{ W}/\text{m}^3$) and superior conversion efficiency (13.86%). Gentle human finger imparting onto the PNG produces enough electric power to directly illuminate as many as 85 numbers of commercial LEDs and to charge a $2.2 \mu\text{F}$ capacitor upto 22 V within 450 sec. The nanogenerator is successfully exploited to generate electrical power by converting mechanical energy from different human activities. We also

demonstrate high mechanosensing capability of thin, flexible e-skin sensor based on NiO@SiO₂/PVDF nanocomposite. Owing to the high sensitivity the fabricated e-skin sensor can detect precisely the spatio-temporal distribution of pressure stimuli in static and dynamic conditions. e-skin sensor is capable to sense very low level pressure stimuli with short response time. Promising role of e-skin in real time health-care monitoring is assessed where a hand-data glove attached with self-powered e-skin sensors can distinguish movements of different fingers. The spatial distribution of pressure stimuli is also resolved by a sensing matrix containing e-skin sensors as pixels. Moreover the operation mechanical stability of the composites is very high which enables this composite to be used in e-skin sensor and energy harvester applications. Our work verifies the scope of NiO@SiO₂/PVDF nanocomposite in nanogenerator and e-skin applications which are essential components in the field of wearable self-powered electronics, healthcare monitoring and artificial intelligence attached with human body.

Keywords: PVDF nanocomposite; Piezoelectric nanogenerator; Clean energy source; e-skin mechanosensor; Flexible electronics.

Introduction

In modern era, portable devices such as mobile phones, wearable electronic products, rollup displays, actuators and sensors are the essential components in Internet of Things (IoT) technology [1-3]. Rapidly increasing power demands in such devices stimulates the researchers to concentrate on development of environmental friendly, biocompatible, flexible and lightweight energy harvester, capable of harvesting electrical energy from the abundant resources in nature and our daily living systems such as human body movement, touch, walking and talking [4-11]. Recently piezoelectric nanogenerators (PNG) have come to light as a promising green technique for the harvesting of electrical energy from such mechanical energy resources through piezoelectric effect [5,12-13]. On the other hand recently flexible, wearable, bio-inspired electronic skin (e-skin) mechanosensors have demonstrated excellent potential for applications in portable self-powered sensors, health care monitoring, energy and robotics for more faithfully mimicking the human skin [14-17]. To achieve both the targets that is development of piezoelectric energy harvester and e-skin, recently poly(vinylidene fluoride) (PVDF) and its copolymers have received much attention due to their high piezoelectric, high dielectric properties, and fair mechanical strength [5,13,21-22]. PVDF based composites are lightweight, highly flexible, highly sensitive to strain and environment friendly in nature. Among the five different phases (α , β , γ , δ and ϵ) of semicrystalline PVDF, β polymorph possess superior piezoelectric and ferroelectric properties due to its all 'trans' (TTT) conformation [23-25]. Thus the development of PVDF composites having high fraction of electroactive β polymorph is most desirable for piezoelectric nanogenerators as well as e-skin applications. There are various ways to increase the electroactive β polymorph in PVDF, such as self-polarization technique [23-25], using of external electric poling process [4,25-27], incorporation of oriented nanofillers [28] and

impregnation of nanofillers having inherent high piezoelectric properties [29]. But among these, self-polarization technique may be the most suitable due to its facile, simple and low cost methodology. Recently several works have been reported by incorporating different metal based nanofillers such as ZnSnO_3 [30], ZnO [21], FAPbBr_3 [26], AlO-rGO [5] and graphene-silver [31] in PVDF matrix to obtain enhanced piezoelectric nanogenerator output. But there are many limitations of these nanocomposites based nanogenerators due to the complicated structure, low output voltage, low power density, less durability and requirement of additional poling process by external electric field. On the other hand, as the field of flexible sensor and actuators quickly advances, a wide range of materials have been explored as sensing elements to fabricate e-skin devices, including organic/inorganic matrix arrays [32-33], polymer composites [34] and hybrid composites [35]. To date the sensing capabilities of these devices have been limited by the compromise between selecting materials that are mechanically durable yet also highly sensitive to strain [36-37]. S. K. Ghosh et. al. [17] recently reported a e-skin sensor based on gelatin nanofiber having a mechanosensitivity of about 0.8 V kPa^{-1} . Extremely small weight, such as rice grain (25 mg), copper wire (15 mg) was detected by another e-skin composed of MWCNT/PDMS composite film containing sunflower pollen microcapsules [15]. Q. Hua et. al. [14] very recently reported a human skin inspired highly stretchable and conformable matrix network which can sense very low pressure $\sim 7.3 \text{ Pa}$ and has a pressure sensitivity of 22.4 MPa^{-1} ($<16 \text{ kPa}$ pressure region). Especially the development of self-powered e-skin has been initiated in the last couple of years due to their vast potential applications in remote mechanosensing to mimicking the human skin [17-20].

Metal oxide nanoparticles including NiO [38], CuO [24], ZnO [21], CoFe_2O_4 [39-40] have great potential to enhance the β phase fraction in PVDF composite, which can be exploited to fabricate

piezoelectric nanogenerators as well as e-skin. Different metal oxide based magnetoelectric polymer composite [39-40] were also studied for enhancement of piezoelectric and ferroelectric properties. But incorporation of metal oxide nanofillers in PVDF matrix is limited by the agglomeration and conductive path formation of the nanofillers, hence high amount of metal oxide nanofiller loading in PVDF is not viable. To resolve the agglomeration and low percolation threshold problems NiO nanoparticles could be coated by non-conductive SiO₂ before adding into the polymer. SiO₂ coating on NiO nanoparticles may retard agglomeration of the NiO nanoparticles in PVDF matrix resulting discrete and homogeneous dispersion of the nanofiller in polymer matrix at a high loading fraction. That may facilitate enhancement of the electrical properties of the composites and eventually enhance the performance of the nanogenerator and tactile e-skin mechanosensor. But to the best of our knowledge no work has been reported on NiO based or silica coated metal oxide /PVDF nanocomposite based piezoelectric nanogenerators and e-skin so far.

In this work, we present fabrication and performance analysis of a novel flexible high performance piezoelectric nanogenerator and a tactile e-skin mechanosensor based on self-polarized NiO@SiO₂/PVDF nanocomposite. The structural, mechanical, thermal and electrical properties of the NiO@SiO₂/PVDF composites were investigated rigorously. The performance of the fabricated nanogenerator was investigated in terms of output voltage, output current, output power and conversion efficiency. Fabricated tactile e-skin mechanosensor was used to detect variable static and dynamic pressure stimuli and spatial distribution of pressure.

Experimental:

Materials

Poly(vinylidene fluoride) (PVDF) pellets ($M_w = 27500 \text{ g mol}^{-1}$) were obtained from Sigma Aldrich, USA. Dry N, N, dimethylformamide (DMF; Merck, India), nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $M_w = 237.69 \text{ g mol}^{-1}$; Merck, India), sodium hydroxide (NaOH; Merck, India) and ethyl alcohol ($\text{C}_2\text{H}_6\text{O}$; Merck, India), tetraethyl orthosilicate (TEOS; Merck, India), ammonia solution 25% (NH_4OH ; Merck, India) were used in this work. All the materials were used in the experiments without further purification.

Synthesis of silica coated nickel oxide ($\text{NiO}@\text{SiO}_2$) nanoparticles

The nickel oxide nanoparticles were synthesized using hydrothermal method [38]. Details of the hydrothermal procedure for synthesis of metal oxide nanomaterials can be found elsewhere [24]. Silica coated nickel oxide nanoparticles ($\text{NiO}@\text{SiO}_2$) were synthesized by modified Stöber [41] method, a widely used method for synthesis of silica nanoparticles. In this typical synthesis procedure, hydrothermally synthesized nickel oxide nanoparticles [38] were added to the solution of water and ethyl alcohol (in volume ratio $\sim 4:1$). To achieve a well dispersed mixture, the solution was sonicated for 10 minutes. After that ammonia was added to the mixture (in volume ratio $\sim 1.4:50$) drop by drop to catalyze the nickel oxide nanoparticles in alcoholic media. The mixture was again sonicated for 40 minutes after the addition of ammonia and finally TEOS was added drop by drop to the mixture (in volume ratio $\sim 0.4:50$). The final mixture was kept under strong magnetic stirring (500 rpm) for 18 hours. The well mixed colloidal solution was centrifuged at 4000 rpm and washed by ethanol to remove the residuals from the product. The collected product was dried at 80°C and employed for further characterization.

Preparation of NiO@SiO₂ loaded PVDF nanocomposite films

The silica coated nickel oxide nanoparticles incorporated PVDF (NiO@SiO₂/PVDF) films were prepared by the simple solution casting method [42]. In the synthesis procedure, at first 500g of PVDF was dissolved in 10ml DMF by magnetic stirring at 60°C. Thereby a certain weight percent (1 wt%, 3 wt%, 5 wt%, 10 wt% and 15 wt%) of the synthesized NiO@SiO₂ nanoparticles were added to the solution of PVDF and strongly stirred for 16 hours. To get a homogeneous mixture, the solution was sonicated for 30 min. Finally the nanocomposite films were prepared by casting the mixture in a Petri dish and it was heated at 90°C till the complete evaporation of the solvent. Neat PVDF (P0) films were also prepared by following the same procedure. The details of the synthesized samples (PSNO1, PSNO3, PSNO5, PSNO10, and PSNO15) are given in the Table-S1 in supporting information section.

Fabrication of nanogenerator based on NiO@SiO₂/PVDF nanocomposite

Sandwich like structure based polymer composite nanogenerators (PNG) were fabricated by placing the NiO@SiO₂/PVDF film (thickness of the film $200 \pm 5 \mu\text{m}$) in between two flexible adhesive carbon tape electrodes (dimension of $1.6 \times 2.5 \text{ cm}^2$). Two copper wires were extended out from the both electrodes and then the whole sample was laminated using Teflon and one sided adhesive tape. Lamination is made to protect the device from external physical damage. The corresponding schematic diagram with digital photographs is presented in Fig. 1, which reflects construction procedure of PNG as well as its flexibility. Figure also shows the flexibility of the self-standing nanocomposite film.

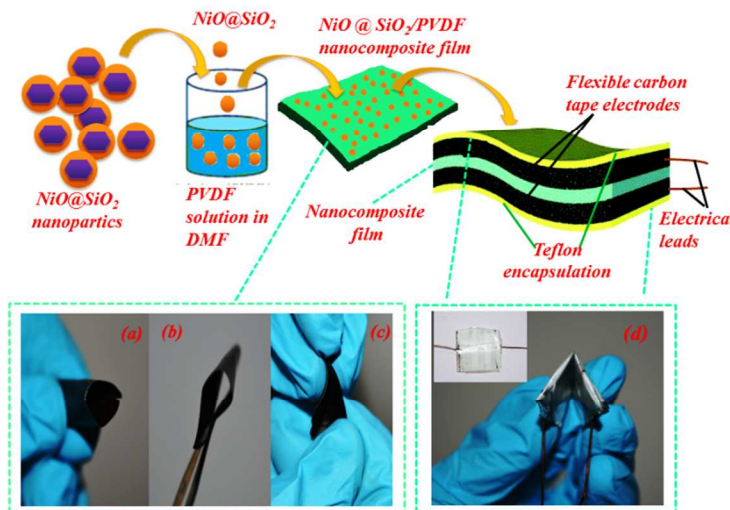


Fig.1: Schematic of the fabrication procedure of NiO@SiO₂/PVDF based nanogenerator. (a-c) NiO@SiO₂/PVDF nanocomposite film with high flexibility (d) fabricated flexible nanogenerator.

Result and discussion:

Silica coated nickel oxide nanoparticles

X-ray diffraction (XRD) analysis. Fig.S1 (supporting information) shows the X-ray diffraction (XRD) pattern of the synthesized silica coated nickel oxide nanoparticles. The well crystalline nature of the sample is evident from the pattern proving the presence of crystalline nickel oxide in the product. The diffraction peaks positioned at 2θ values 37.03° , 43.16° , 62.71° and 75.19° are indexed to the (101), (012), (110), and (113) and (202) crystalline planes of rhombohedral nickel oxide (NiO) ($a = 2.955 \text{ \AA}$, $c = 7.2275 \text{ \AA}$) in accordance with the JCPDS no. 44-1159. Moreover a well recognizable hump within the range of 15° to 30° is observed due to the presence of amorphous silica in the product.

Electron microscopy analyses. The transmission electron microscopy (TEM) micrograph of the well dispersed silica coated nickel oxide nanoparticles is shown in Fig.2. The NiO nanoparticles

are properly coated with silica with well-defined boundaries. Inset (bottom) of the figure shows the high magnification image of NiO@SiO₂ nanoparticles. Lighter amorphous silica cell around the darker mono-disperse NiO nanoparticle is distinctly visible in the figure. Another inset (top) of the figure shows the selected area electron diffraction (SAED) pattern of NiO@SiO₂ nanoparticles. The 'Dot' patterned SAED result depicts the single crystalline nature of the NiO nanoparticle. The d-spacing values obtained from the SAED pattern are 2.423 nm, 2.096 nm and 1.483 nm corresponding to the (101), (012) and (110) planes of NiO crystals (JCPDS no. 44-1159) respectively. The presence of hollow spheres in the SAED pattern reflects the amorphous silica coating.

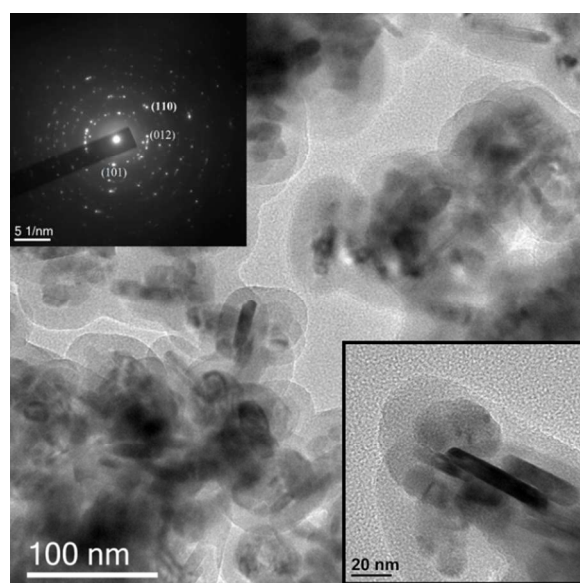


Fig.2: HRTEM image of the silica coated nickel oxide nanoparticles. Insets of the figure show the SAED pattern and high magnification image of the NiO@SiO₂ nanoparticles.

Nickel oxide loaded PVDF nanocomposite films

X-ray diffraction (XRD) analysis. X-ray diffraction (XRD) spectroscopy of the neat PVDF and NiO@SiO₂ nanoparticles loaded PVDF composites was performed to quantitatively study the polymorphism of PVDF. Fig.3a shows the XRD pattern of the neat PVDF (P0) and NiO@SiO₂

/PVDF nanocomposite films (PSNO3, PSNO5, PSNO10 and PSNO15). The diffraction pattern of the neat PVDF (P0) shows the semi-crystalline nature of the polymer. The peaks positioned at 2θ values of 17.5° (100), 18.2° (020), 19.7° (021), and 26.6° ((201), (310)) of the neat PVDF can be ascribed to the nonpolar α phase of PVDF [23-25,38]. For NiO@SiO₂/PVDF nanocomposite, two well recognized peaks positioned at 2θ values of 36.95° and 43.02° can be indexed to the (101) and (012) crystal planes of rhombohedral NiO (JCPDS no. 44-1159), which confirms the presence of the NiO in the PVDF matrix. The presence of the silica in the composite could not be distinguished prominently in the figure as the hump like pattern of the silica in XRD pattern was overlapped with the semicrystalline hump of the PVDF matrix itself in the 15° to 30° range of 2θ . It is evident from the figure that with increasing loading fraction of NiO@SiO₂ nanoparticles in PVDF matrix, the relative intensity of the peaks corresponding to the α phase of PVDF (positioned at 17.5° , 18.2° , 19.7° and 26.6°) decreases prominently. However, for the PVDF nanocomposite films a new peak appears at 2θ values of 20.3° ((020),(101)) which can be ascribed to the characteristic peak of β phase of PVDF [20]. This phenomena infers that the loading of the NiO@SiO₂ nanoparticles in the PVDF matrix causes transformation from the nonpolar α phase to polar β phase of PVDF [23-25,38]. The XRD pattern also shows a peak positioned at 2θ value of 38.9° (211) corresponding to the γ phase of PVDF in the neat as well as loaded PVDF films [23-25,38]. Fig.S2 shows the filler dependence of the parameter ($I_{20.3^\circ}/I_{18.2^\circ}$) calculated by taking the ratio of two peak intensities positioned at 20.3° (characteristic peak for β phase) and 18.2° (characteristic peak for α phase). This ratio ($I_{20.3^\circ}/I_{18.2^\circ}$) reveals the β and α phase fraction in the NiO@SiO₂/PVDF nanocomposites. The ratio is about 0.93 for the neat PVDF film and this ratio is gradually increased with the increasing loading of filler in PVDF matrix. The maximum value of this ratio is achieved for the sample PSNO15, which is about

1.55. Henceforth the XRD patterns of the nanocomposite films confirm that the incorporation of the NiO@SiO₂ nanofillers successfully transforms the nonpolar α phase fraction to the polar β phase of PVDF.

Field emission scanning electron microscopy (FESEM). Fig.S3 (supporting information) shows the FESEM micrograph of neat PVDF. The neat PVDF possesses a highly compact and uniform surface morphology with well-recognizable (marked by red circles) spherulites having average diameter $\sim 10\ \mu\text{m}$. Fig.3b shows the surface morphology of the sample PSNO15 where uniform distribution of the spherulites (marked as red circles in the figure) having average diameter $\sim 3\ \mu\text{m}$ is observed throughout the entire surface of the composite film. These uniformly distribution of spherulites confirms the homogeneous dispersion of NiO@SiO₂ nanofillers in the PVDF matrix for the sample PSNO15. The average diameter of the spherulites for the sample PSNO15 is much smaller than the neat PVDF reflecting the faster nucleation kinetics in NiO@SiO₂ /PVDF nanocomposite film [24,38,43]. The NiO@SiO₂ nanoparticles acted as nucleation centers in PVDF matrix, resulting the enhancement of the β phase fraction of the nanocomposite films as well as faster nucleation kinetics. Inset of the Fig.3b shows the high magnification FESEM micrograph of the nanocomposite film. Red line mark in the inset represents the impinging of spherulites which is occurred due to the faster nucleation kinetics. Hence the FESEM micrographs support the enhancement of the electroactive β phase in PVDF via the incorporation of the NiO@SiO₂.

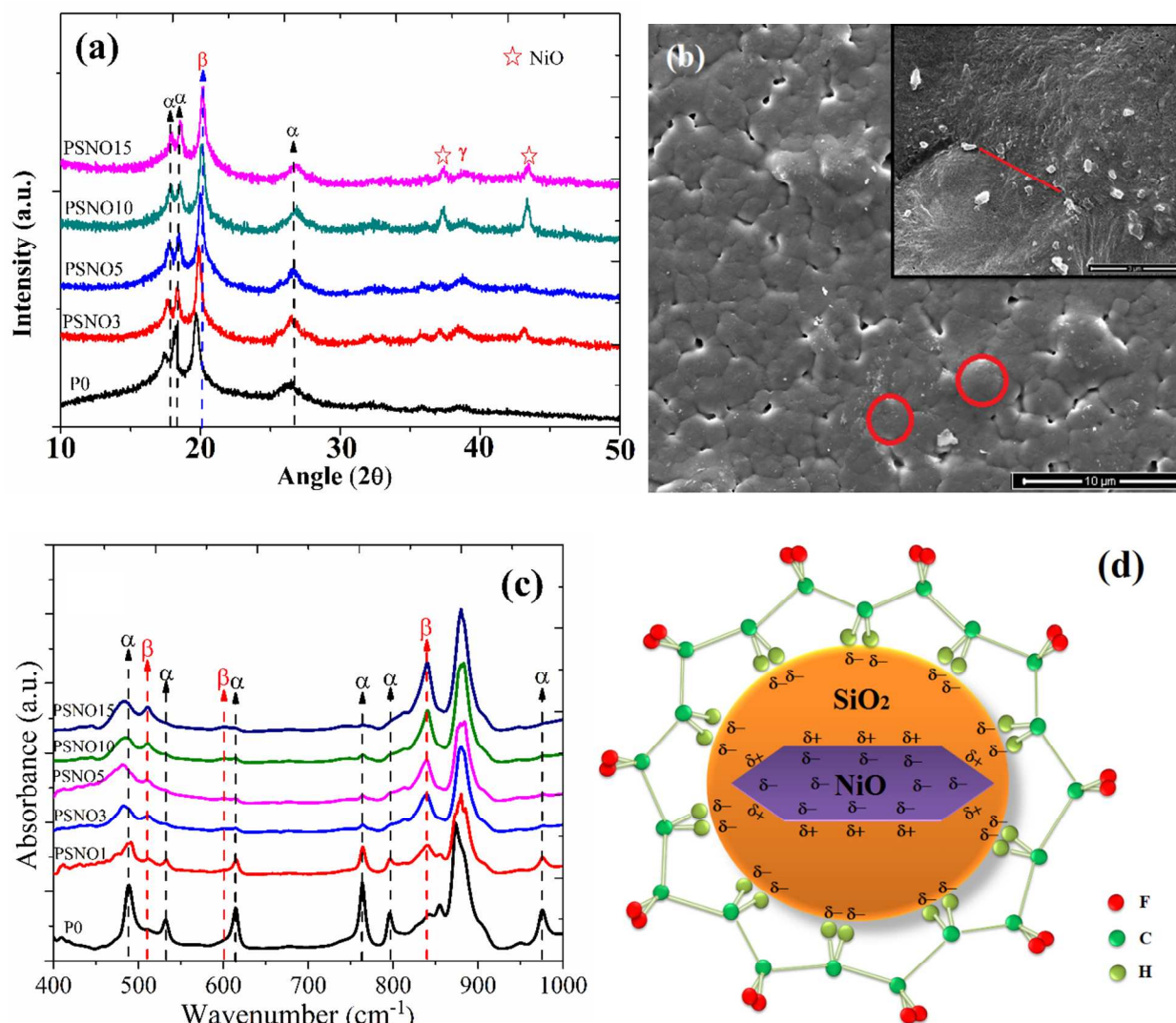


Fig.3: (a) XRD patterns of the neat and NiO@SiO₂ nanoparticles loaded PVDF films; (b) FESEM micrograph of the PSNO15; Inset of the figure shows the high magnification image of PSNO15; (c) FTIR spectra of the neat PVDF (P0) and NiO@SiO₂ nanoparticles loaded PVDF films (PSNO1, PSNO3, PSNO5, PSNO10 and PSNO15); (d) Schematic of the proposed β phase formation mechanism.

Fourier Transform Infrared Spectroscopy. Fourier transform infrared (FTIR) absorption spectra of neat PVDF and NiO@SiO₂/PVDF nanocomposite films (PSNO1, PSNO3, PSNO5, PSNO10 and PSNO15) are shown in Fig.3c. The FTIR spectrum of the neat PVDF shows

characteristic peaks positioned at 488cm^{-1} (CF_2 wagging), 532cm^{-1} (CF_2 bending), 615cm^{-1} and 764cm^{-1} (CF_2 bending and skeletal bending), 796cm^{-1} and 976cm^{-1} (CH_2 rocking) ascribed to the IR bands of nonpolar α phase of PVDF [23-25,38]. Figure depicts that the relative intensity of absorption bands corresponding to nonpolar α phase of PVDF are gradually decreased with increasing NiO@SiO_2 loading in PVDF matrix. It is evident from the figure that for sample PSNO15, all the peaks corresponding to α phase are almost completely diminished, only the characteristic peaks assigned to polar β phase appear prominently at 510cm^{-1} (CF_2 stretching), 600cm^{-1} (CF_2 wagging), 840cm^{-1} (CH_2 rocking, CF_2 stretching and skeletal C-C stretching) [23-25,38]. Hence, the FTIR results indicate that there is a significant non polar α to polar β phase transformation of PVDF is occurred with the loading of the NiO@SiO_2 nanoparticles in the PVDF matrix. β phase fraction ($F(\beta)$) is quantitatively estimated for the neat and nanocomposite films using equation (S1) of supporting information. Fig.S4 (supporting information) shows the variation of $F(\beta)$ with NiO@SiO_2 nanoparticles loading in PVDF matrix. Figure shows that with increasing loading fraction of the NiO@SiO_2 nanoparticles in PVDF matrix the $F(\beta)$ increases. The maximum value of $F(\beta)$ is 80%, achieved for 15 wt% NiO@SiO_2 nanoparticles loading. The interaction between the filler and the polymer matrix leads to this enhancement of β phase fraction with the filler loading. When the filler content is low the effective interfacial area between the polymer and the NiO@SiO_2 nanoparticles is less. With the increment of the loading of homogeneously dispersed NiO@SiO_2 nanoparticles in the polymer matrix the interfacial area also increases leading to the increment of the number of aligned chains having 'all trans' conformation. Hence there is a successful increment of the electroactive β phase fraction by NiO@SiO_2 nanofiller and the sample PSNO15 with maximum β phase fraction may be chosen as an ideal candidate for the flexible piezoelectric nanogenerator device fabrication.

This enhancement of the electroactive β phase in the nanocomposite films can be assigned to the electrostatic interaction between the negatively charged surface of NiO@SiO₂ nanoparticles (Fig.S6, Supporting Information) and positive $-\text{CH}_2$ group of PVDF [24,43-46] as shown in the schematic of Fig.3d. The detail evidences and discussions regarding the β phase formation through surface charge - dipole ($-\text{CH}_2$ group) interaction are provided in the supporting information sections (S2.1 and S2.2).

Dielectric properties.

Fig. 4 shows the frequency dependent dielectric properties of the NiO@SiO₂ loaded PVDF films at room temperature and atmospheric pressure. At 20 Hz dielectric constant of value 110 is achieved for 15 wt% of NiO@SiO₂/PVDF nanocomposite, which is about 15 times greater than that of the neat PVDF film. The enhancement of dielectric constant can be explained by the Maxwell–Wagner–Sillars (MWS) interfacial polarization mechanism [23,38,43]. When an electric field is applied, the space charge accumulation and short-range dipole–dipole interactions at the interfaces of the NiO@SiO₂ and PVDF results in large interfacial polarization as well as large dielectric constant at lower frequency region. The dielectric constant (ϵ) decreases with increasing frequencies for neat as well as nanocomposite films. This phenomenon is occurred due to the decrease in number of aligned dipoles with increasing frequency [23,38,43]. When the frequency is low ($\omega \ll 1/\tau$), where τ is the relaxation time, the orientation of the dipoles can follow the field but when the frequency of the external field increases ($\omega < 1/\tau$), the dipoles begin to lag with the field. At high frequency region ($\omega \gg 1/\tau$), the dipoles can no longer follow the electric field and the dielectric constant decreases. Fig.S7a (supporting information) shows the frequency dependence tangent loss ($\tan \delta$) of the neat and nanocomposite

films. It can be clearly seen from the figure that the tangent loss increases with the loading of the NiO@SiO₂ and for PSNO15 the corresponding value is ~0.28 at 100 Hz.

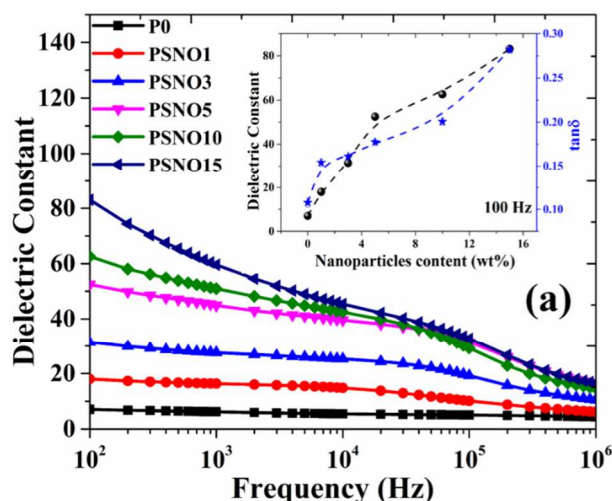


Fig.4: Variation of dielectric constant with frequency of the samples P0, PSNO1, PSNO3, PSNO5, PSNO10 and PSNO15. Inset of figure shows the variation of dielectric constant and dielectric loss with loading concentration at (100Hz).

The variation of dielectric constant and dielectric loss (at 100Hz) of the NiO@SiO₂ loaded PVDF composites with the variation of nanoparticles content is shown in the inset of Fig.4. The figure depicts that the dielectric constant increases with the increment of the NiO@SiO₂ loading in PVDF matrix. Maximum value of dielectric constant c.a. 83 at 100 Hz is achieved at 15wt% loading of NiO@SiO₂ (PSNO15). The enhancement of dielectric properties can be extensively explained by two major phenomena. First one is the MWS interfacial polarization effect. This type of interfacial polarization appears for heterogeneous medium consisting of different phases having dissimilar permittivity and conductivity, which causes accumulation of the charges at the interfaces [23,38,43]. With the increment of the nanofillers content, the number of nanofillers and total interfacial area per unit volume are increased which in turn reduces the inter-particle

distance. This improves the average polarization associated with the nanofillers and the coupling between neighboring grains of polymer leads to the enhancement of dielectric constant of the nanocomposite films. The other responsible phenomenon is the enhancement of electroactive β phase content in the polymer nanocomposite films by incorporating NiO@SiO₂ in PVDF matrix, due to which the dielectric property of the nanocomposite films are also enhanced.

Fig S7b-c show the variation of dielectric constant and loss with frequency in different temperature for the sample PSNO15. Figures show that with the increment of the temperature the dielectric constant and loss increased and at temperature 423 K the dielectric constant is about 170 and loss is about 0.98 at frequency 40 Hz. The frequency dependence of tangent loss of the sample PSNO15 (Fig.S7c) shows a relaxation region in the 10² to 10⁵ Hz frequency domain which may be assigned to the α_c type of relaxation [47]. The relaxation peaks, related to the α_c relaxation process show increment in magnitude with the increasing temperature and shift toward higher frequency, as well.

Piezoelectric nanogenerator

Piezoelectric nanogenerator performance:

The nanogenerator scavenging human body motion based energy was fabricated by simple electrode—self-standing composite film—electrode sandwich structure avoiding any critical, complex fabrication process like TENG [48-49] or PNG-TENG hybrid [50] devices .The piezoelectric energy harvesting performance of the fabricated NiO@SiO₂/PVDF composite based nanogenerators (PNGs) was investigated under periodic vertical compressing and releasing process. The periodic compressing pressure was exerted onto the top surface of the nanogenerators by human finger imparting of peak amplitude ~ 0.3 MPa (pressure calculation is shown in section S2.5 of supporting document) at a frequency of ~4 Hz as shown in video VS1

of supporting information. The active area for testing of the nanogenerators was $(1.6 \times 2.5) \text{ cm}^2$. Under the exertion of that periodic, vertical and simple biomechanical stress the nanogenerators generate the time varying voltage and current signals accordingly and serve as efficient energy generation sources. Study on optimization of $\text{NiO}@\text{SiO}_2$ filler loading in PVDF matrix was carried out to find out the most suitable candidate for energy harvesting application. Fig.S10 shows the variation of the output voltage with $\text{NiO}@\text{SiO}_2$ filler loading in PVDF matrix. PNG15 containing PSNO15 composite film exhibits highest piezoelectric output voltage as it possesses highest electroactive β phase content. As a promising outcome the PNG15 can produce output voltage upto $\sim 53 \text{ V}$ across $30 \text{ M}\Omega$ load resistance. Fig.5a shows the time varying output voltage generated from PNG15 under $\sim 0.3 \text{ MPa}$ external stress at $30 \text{ M}\Omega$ load resistance. The magnified view of one complete cycle of output voltage is shown in Fig.5a, which reveals two sets of responses of positive and negative piezoelectric potentials. The first as well as the most prominent positive peak is generated from the direct impact of the external stress; while the first negative peak corresponds to the releasing effect. This negative peak occurs at the time when device changes from a compressed state to a relaxed state after removal of the initial stress. The later set of piezoelectric potentials can be attributed to the damping effect in the nanocomposites film [26]. In the both sets, the sharp difference between positive voltage peak and negative voltage peak is distinctly observed due to the different straining rate of $\text{NiO}@\text{SiO}_2/\text{PVDF}$ nanocomposite film corresponding to the compression and releasing processes [51]. Fig.S11 shows the rectified output voltage of the PNG15. The magnified view of one cycle of the rectified voltage signal shows four peaks corresponding to two positive peaks and two negative peaks of non-rectified signal. The self-polarized [5,21] 15 wt% $\text{NiO}@\text{SiO}_2/\text{PVDF}$ based nanogenerator exhibits an outstanding output performance with a maximum rectified voltage of

53 V at 30 M Ω load resistance, without involving any external poling process of the nanocomposite film.

The measured time varying short circuit current (rectified) of PNG15 is shown in Fig.5b. An instantaneous current of peak value as high as 1.2 μ A is achieved for PNG15. The variation of measured current density (current/area) generated from PNG15 with increasing load resistance is shown in Fig.5c. A maximum current density of 0.3 μ A/cm² is achieved at 1 K Ω resistance and the amplitude of the current density decreases with increasing load resistance due to ohmic loss. It is well known that the potential of a nanogenerator in real life applications depends on its power generation capability. The variation of output voltage and instantaneous power density (power density = power/volume = $\frac{V \times I}{area \times thickness}$) across different load resistance (R_L) is shown in Fig.5d. The amplitude of the output voltage increases with the increasing load resistance and is almost saturated after 30 M Ω load. The voltage reaches at the peak value of 53 V at 30 M Ω load, which is considered as open circuit voltage at theoretically infinite high resistance. Maximum power was obtained across the load resistance of 10 M Ω and the value of the output power density is 682 W/m³ at optimum power transfer condition. To the best of our knowledge, under similar experimental condition the power density of our PNG is quite high in comparison to other similar devices [5,26,29].

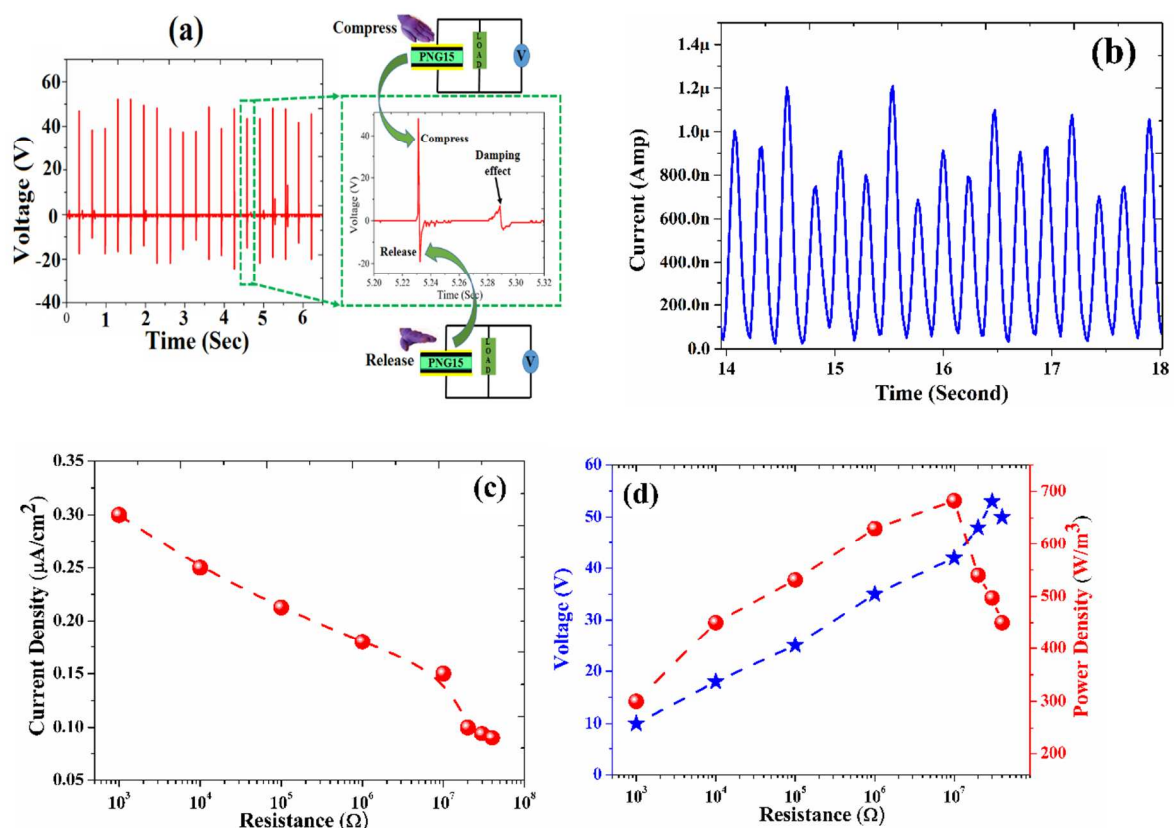


Fig.5: (a) Time varying piezoelectric output voltage of the PNG15 made-up with PSNO15 film while external periodic vertical compression was provided by finger imparting onto the PNG15. Enlarged view of the figure shows one cycle of the output voltage and rectified output voltage. The corresponding circuit diagram in compress and release conditions are given with the enlarged views of the cycles; (b) Time varying short circuit current of PNG15; Variation of (c) surface current density; (d) average piezoelectric output voltage and corresponding power density of the PNG15 with different load resistances.

To have a direct idea about the energy producing capability of the PNG15, a capacitor of 2.2 μ F was charged via a full wave rectifier where input mechanical energy to the nanogenerator was supplied by the gentle human finger imparting. The gradual charging of the capacitor via the PNG15 generated power (rectified) under periodic compression and release procedure is shown

in Fig.6a. The voltage across the 2.2 μF reaches at 22 V within only 480 s under the biomechanical pressure of ~ 0.3 MPa at a frequency of ~ 4 Hz and reaches at steady state condition within 480 s. Based on the charging capability of the NG, the stored energy in the capacitors is also calculated by $E_c = 1/2 CV^2$ and the value is 532.4 μJ for 2.2 μF capacitor for the 1920 numbers of charging cycles during 480 s. It is noteworthy that this high charging performance of the PNG15 is achieved without the application of any external poling of nanocomposites film or triboelectric process. Piezoelectric efficiency or energy conversion efficiency of the PNG15 is calculated by the equation $\eta = \frac{W_{out}}{W_{in}}$ (detail of the calculation procedure is mentioned in S2.5 of supporting document), where W_{out} is the output electrical energy stored in capacitor (E_c) and W_{in} is the input mechanical energy. The efficiency of the PNG15 is found to be 13.86%. This high piezoelectric efficiency strongly suggests the viability of use of self-polarized NiO@SiO₂/PVDF nanocomposite based flexible, facile piezoelectric nanogenerators in real life applications and large scale production. The efficiency of our fabricated nanogenerator is superior to other recently reported piezoelectric nanogenerators as mentioned in Table-I.

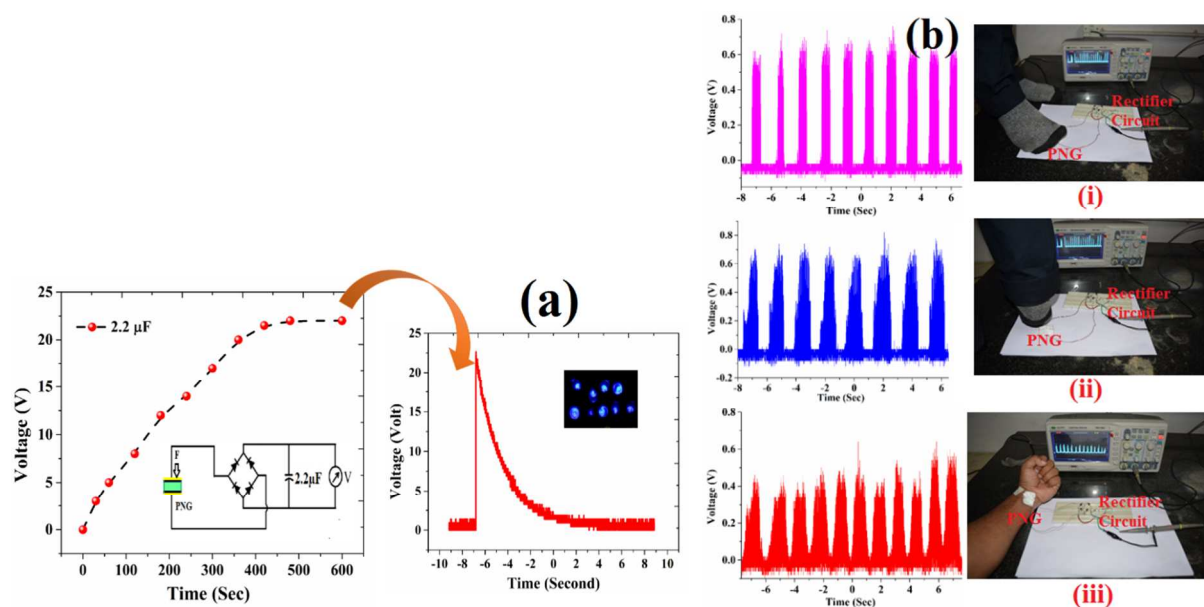


Fig.6: (a) Charging of the 2.2 μF capacitor by the power generated from the PNG15 under periodic finger imparting process using a full wave rectifier. Inset shows the circuit diagram for charging the capacitor. The pointed figure shows discharging of the capacitor recorded by the digital storage oscilloscope and the corresponding power of capacitor was used to turn on 9 LEDs; (b) Digital image of piezoelectric power generation (rectified output voltage) by PNG15 due to (i) toe pressure, (ii) heel pressure, (iii) wrist bending.

Fabricated PNG15 was exploited to harvest human body motion based energy. Power generation capability of the PNG15 due to the different human body parts movements including movement of toe, heel and wrist (along with finger imparting) was investigated to establish the real life applications of the flexible nanogenerator under biomechanical pressure. The digital images of piezoelectric power generation by the fabricated PNG15 due to different human body parts movement are shown in Fig.6b. Gentle movement of toe onto the top surface of NG generates 0.6 V output as shown in Fig.6b (i). PNG15 produces 0.6 V and 0.5 V output due to the gentle pressure from heel (Fig.6b (ii)) and the bending of wrist (Fig.6b (iii)) respectively. Video VS2

(supporting information) shows the rectified piezoelectric output from PNG15 due to the movement of human heel, toe and wrist twisting. Generation of electric power through human finger imparting was recorded in DSO as shown in video VS1 (supporting information). A panel containing as many as 85 commercial blue and yellow LEDs is directly powered from the PNG15 using gentle finger imparting as input mechanical energy, a rectifier circuit was used to supply the rectified power to the panel. Video VS3 in supporting information shows all the LEDs are instantly illuminated in synchronization with finger impact on the nanogenerator.

Table-I: Comparison of performance of PNG15 with the other previously reported piezoelectric nanogenerators.

Nanogenerator	Energy conversion efficiency (%)	Peak Voltage (Volt)	Current Density/ Short Circuit Current	Power/Power Density	Ref
ZnO/PVDF	2.61	24.5	1.7 μA	32.5 mW/cm^3	[21]
FAPbBr ₃ /PVDF	0.55	30	6.5 $\mu\text{A}/\text{cm}^2$	27.4 $\mu\text{W}/\text{cm}^2$	[26]
Li@ZnO/PDMS	-	30	7 μA	-	[3]
AlO-rGO/ PVDF	9.25	36	0.8 μA	27.9 $\mu\text{W}/\text{cm}^3$	[5]
BaTiO ₃ /PVDF-TrFE	-	0.11	-	25 μW	[27]
Ce ³⁺ /Graphene/PVDF	-	11	6 nA/cm^2	-	[4]
NiO@SiO₂/PVDF	13.86	53	0.3$\mu\text{A}/\text{cm}^2$	685 W/m^3	This work

The superior performance of the fabricated PNG15 is obviously attributed to the flexible, self-polarized 15 wt% NiO@SiO₂/PVDF composite film having high β phase fraction (78%) which is induced by surface charge of the silica coated nickel oxide nanoparticles (NiO@SiO₂). Surface charge induced β phase formation is a typical self-polarization technique where the PVDF molecules are properly oriented around the surface of silica coated nickel oxide nanoparticles without application of any energy consuming, complex external electrical poling process. Essentially the silica coating on NiO nanoparticles resists the coagulation of the NiO

nanoparticles even at high filler loading condition, and uniform and discrete dispersion of the NiO@SiO₂ nanoparticles in the PVDF matrix enhances the interfacial area between the nanofillers and polymer matrix. That plays the key role for the formation of high fraction of polar β phase. Silica coating on NiO nanoparticles also helps to retard the formation of NiO conducting path within the PVDF matrix even at higher nanofiller loading fraction and increases the dielectric constant (83 at 100 Hz) of the PSNO15 composite maintaining low $\tan\delta$ value (0.28 at 100 Hz). That rightly causes low leakage current through the film enabling efficient piezoelectric nanogenerator applications of the composite.

Fabricated metal oxide based inorganic-organic piezoelectric energy harvester generates electrical signal by scavenging ambient mechanical energy which is supplied by human motion based energy in this work. Working mechanism of the NiO@SiO₂/PVDF composite based nanogenerator having high β phase fraction is the typical application of fundamental piezoelectric theory. The schematic representing the electrical signal generation through dynamic compression-release process is illustrated in Fig.7. In consistent with basic piezoelectric theory, the stress induced piezoelectric potential [22,52] across the electrodes (attached with the self-polarized PVDF composite film) is responsible for this electrical signal generation, which can be described in the following steps. Step-I, initially the net dipole moment of the NiO@SiO₂/PVDF composite is zero in absence of any external mechanical force and the electrical output of the nanogenerator is zero. In step-II, the total dipole moment of the composite film changes along the direction of applied vertical compressive force and a piezoelectric potential across the electrodes is developed. External positive and negative charges from the connected wires are accumulated at the electrodes to screen this piezoelectric potential, consequently the first positive electrical signal is generated from the nanogenerator. Step-III, with the withdrawing of the

vertical compressive force the vertical strain and the piezoelectric potential across the electrodes is diminished. As a result, the accumulated charges are transported back in a reverse direction and the first negative electrical signal is generated. The second set of electrical signals containing weak positive and negative voltage peaks (as shown in Fig.5a) are generated due to the elastic restoring force in the polymer matrix, which causes damped vibration of the polymer film. As a consequence, again a weak piezoelectric potential across the electrodes is developed and motions and accumulation of the charges are occurred via the electrodes similar to the main signals. This results two back to back weak positive and negative peaks.

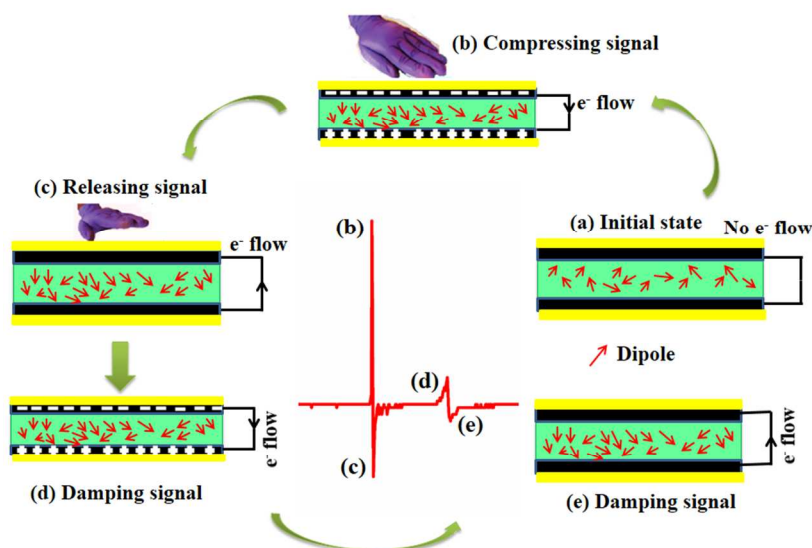


Fig.7: (a) Random orientation of the electric dipoles in the NiO@SiO₂/PVDF film at initial condition, (b) when the compressive force is applied on the NG, piezoelectric potential is generated and electron flow is occurred (c) as soon as the compressive force released, the accumulated electrons flow back in the reverse direction resulting reverse piezoelectric signal (d) a weak forward piezoelectric potential is generated and electron flow is occurred due to damping effect (e) after recovering from the damping effect NG returns to original state, again a reverse

piezoelectric signal is generated. The inset is the enlarged view for one cycle of output voltage under forward connection corresponding to Fig.5a.

The mechanical durability of the PNG15 was investigated over 8 weeks (~ 2400 cycles in 600 sec in each span, ~ 25 min/day) under periodic compressing and releasing process of driving stress of 0.3 MPa at a frequency of ~ 4 Hz. Still after eight weeks and total 360,000 cycles of compression-relaxation PNG15 shows much satisfactory result without exhibiting any degradation in output voltage as shown in Fig.S14b (Supporting Information). The eight weeks used PSNO15 film was able to withstand the external mechanical force for the eight weeks and did not show any notable degradation in mechanical property even after exhaustive use of the film. In Fig.S14a (Supporting Information) the stress-strain plot of the eight week used PSNO15 film shows that the value of Young modulus of the used film is almost same as the initial one. This indicates the high endurance of the nanogenerator even after exhaustive applications. The overall performance and durability of the fabricated nanogenerator prototype based on NiO@SiO₂/PVDF composite indicates that the material is suitable for large scale production of piezoelectric energy harvesting device due to its high efficiency, high mechanical durability, low cost and simple fabrication pathway.

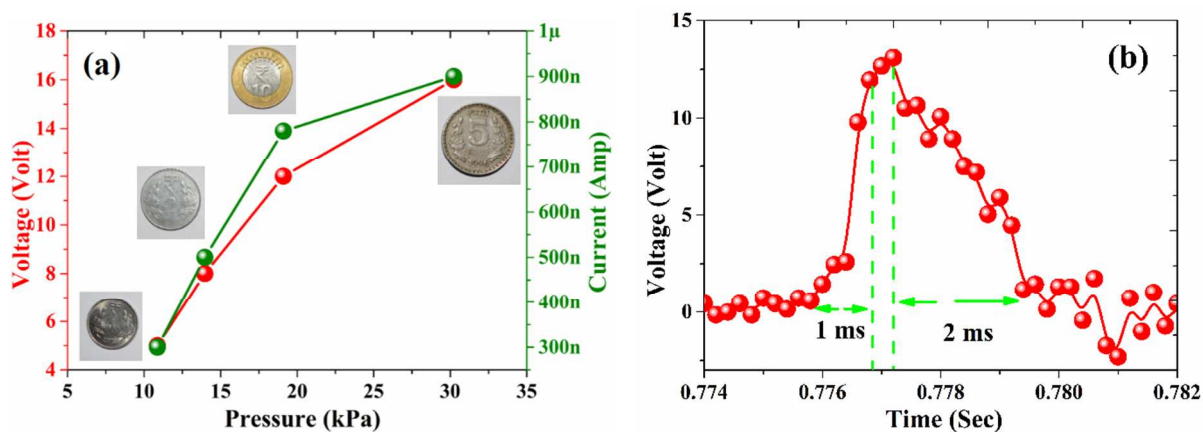
Mechanosensing properties of e-skin:

Fabrication

Sandwich like structure based e-skin sensors were fabricated by placing the 15 wt% NiO@SiO₂/PVDF film (thickness of the film 200±5 μm) in between two flexible copper electrodes. Two wires were extended out from both electrodes.

Dynamic pressure monitoring by self-powered e-skin:

Fabricated self-powered e-skin (area $\sim 1.6 \times 2.5 \text{ cm}^2$) was used to monitor variable pressure in a dynamic condition at low pressure region of 10 kPa to 35 kPa. Coins of different weights (3.80 g, 4.89 g, 7.7 g and 9.09 g) were dropped on the e-skin from 10 cm height. Fig.8a shows the corresponding generated signals. Pressure calculation corresponding to coins dropping is mentioned in Table S2 in supporting document. The generated piezo- voltage and piezo-current were increased with increasing pressure (Fig.8a). Output voltage and current as high as 16 V and of $0.9 \mu\text{A}$ are generated at 30 kPa due the dropping of a INR 5.00 coin of mass 8.91 gm. The dynamic pressure sensitivity of the e-skin is calculated as, $=\Delta V/\Delta P$, where ΔV and ΔP are the differences in generated voltage and applied pressure respectively. The quite high dynamic pressure sensitivity ($\sim 0.97 \text{ V kPa}^{-1}$) makes fabricated e-skin sensor suitable candidate for healthcare monitoring, robotics and artificial intelligence applications. The response and relaxation nature of the e-skin is shown in Fig.8b, which shows rapid response and relaxation time of $\sim 1 \text{ ms}$ and $\sim 2 \text{ ms}$ respectively. Which is a much needed criteria for a realistic e-skin sensor.



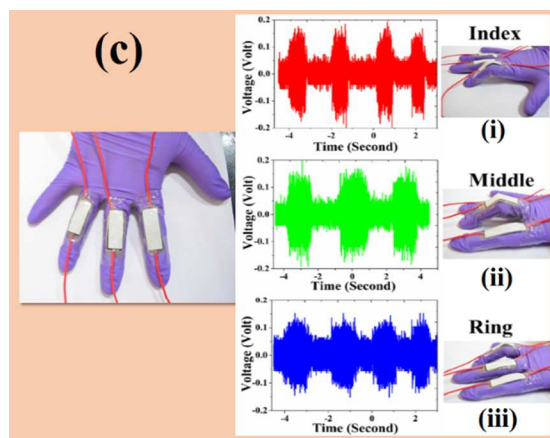


Fig.8: Variation of (a) output voltage and output current of e-skin comprising PSNO15 film with different coin pressure with different coin pressure, (b) Response and relaxation time with voltage; (c) Three e-skin sensors were integrated to index, middle and ring fingers of a health-data glove (right hand). Voltage generation by stretching-bending motion of (i) index; (ii) middle and (iii) ring fingers.

Fine motions of human fingers were distinctly sensed by the fabricated e-skin attached to the fingers. As a proof of concept, three e-skin sensors (area $\sim 1.0 \times 3.0 \text{ cm}^2$) were integrated to a health-data glove (right hand) as shown in Fig.8c, which precisely detected the minute stretching-bending motion of the index, middle and ring fingers. Fig.8c shows the signals for movements of different fingers. Movement of each finger results different and well recognizable signal pattern which may be useful for healthcare monitoring for bed-ridden patients [14-17], controlling master- hand of surgical robot [14-17]. Moreover self-powered e-skin based prototype health-data glove can be used at any portable, flexible condition removing constraint faced by the conventional health-data glove comprising optical fiber or metal strain gauge as sensor elements [18-20].

Static pressure monitoring and mapping by e-skin:

Fabricated e-skin sensor was used to demonstrate successful and precise detection of various static mechanical pressures. The e-skin sensor was employed in passive mode and self-powered mode to detect the static pressure stimuli. In passive mode the e-skin sensor (area $\sim 1.8 \times 1.6 \text{ cm}^2$) registered change in capacitance and impedance depending on the static mechanical pressures in the range of 0.1 kPa to 1.2 kPa. The capacitance of an e-skin sensor increases with increasing static pressure (Fig.9a) and simultaneously the impedance of the device decreases (Fig.9b). Fig.9c shows the linear change in capacitance and impedance with static mechanical pressure indicating successful detection of static pressure. The linear response of the fabricated e-skin sensor is useful for real life tactile mechanosensing applications. Based on the change in capacitance, the static pressure sensitivity (S) of the device can be determined by the relation $S = (\Delta C/C_0)/P$. The obtained sensitivity is 26.58 MPa^{-1} , which is higher than the value reported in recent work of Hua et. al. (22.4 MPa^{-1}) [14]. The e-skin sensor can be exploited to sense very small weight. Loading of a piece of paper of mass 10 mg on e-skin was monitored by recording a 1fF change in capacitance. The sharp increase in capacitance of the e-skin sensor with small change in loading pressure can be attributed to the reduction of distance between the two copper electrodes covering the polymer composite film of adequate flexibility and high dielectric constant [14]. Comparison of the performance of different types of e-skin mechanosensors has been included in Table-S4.

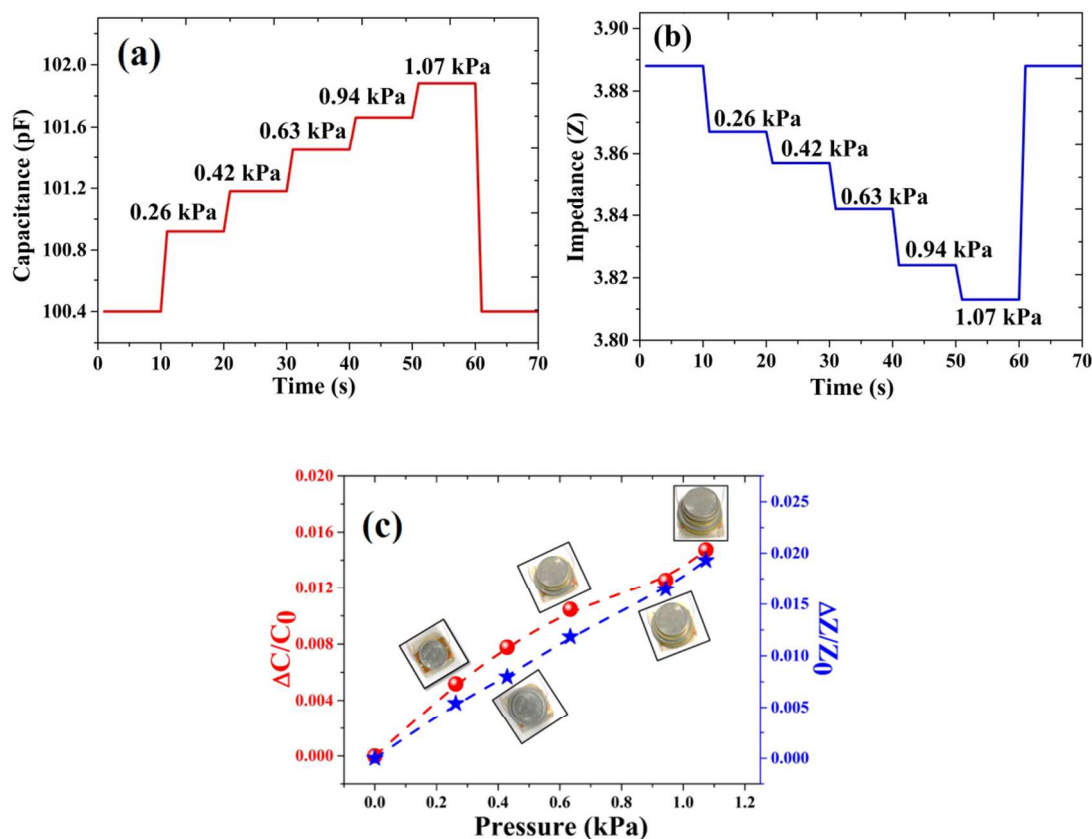


Fig.9: Real time static pressure monitoring during sequential increase in pressure by measuring (a) capacitance and (b) impedance of e-skin, (c) Linear change in capacitance and impedance of the e-skin with change in static pressure.

Large scale application and integration of e-skin depends on its ability to resolve spatial distribution of static pressure for distinguishing shape of different objects. A flexible (3 X 3) pixel sensing matrix with each pixel (sensor) area of 1.2 cm × 1.2 cm was fabricated using a single PSNO15 film with copper tape as electrode to demonstrate the spatial pressure resolution (Fig.10). This sensing matrix is capable of mapping pressure variation due to placing of an object on it. Pressure profile mapping was made in self-powered mode where pressure distribution due to object loading was mapped by measuring generated voltage by each of the pixel of sensing matrix. In passive mode, pressure variation was mapped by measuring change in capacitance of

each pixel due to static pressure. When two fingers were loaded with different pressures on top of the sensor matrix, the pressure variation was readily measured (Fig.10a-c). Pressure distribution was also accurately mapped by the matrix when an object of 'O' shape (mass ~ 2.87 gm) was loaded onto the tactile pressure sensor matrix (Fig.10d-f). The clearly noticeable change in measuring parameters at each pixel for variation of static pressure indicates successful detection of spatially resolved static pressure stimuli and ability to display 2-D projection of object through mechanosensing.

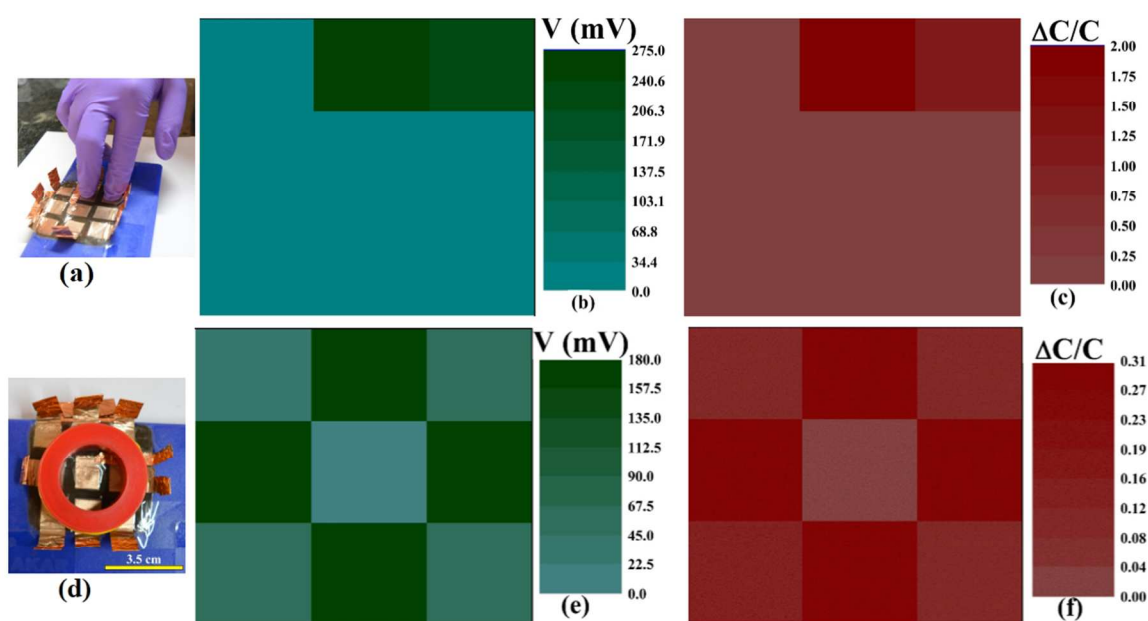


Fig.10: (a) Two fingers are placed on the two upper corner pixels of the sensing matrix and corresponding pressure mapping is shown by (b) voltage generation mapping and (c) change in capacitance mapping; (d) 'O' shaped object is placed on the sensing matrix and corresponding pressure mapping is shown by (e) voltage generation mapping and (f) change in capacitance mapping.

Conclusion:

In summary, we synthesized facile NiO@SiO₂/PVDF nanocomposite and demonstrated the applications of this novel polymer nanocomposite in human body motion based energy harvesting and tactile e-skin mechanosensing. SiO₂ coating on NiO nanoparticles retards agglomeration of the NiO nanoparticles in PVDF matrix. Discrete and homogeneous dispersion of the nanofiller at a high loading fraction helps to enhance the piezoelectric and dielectric properties of the composite, which have been exploited to fabricate the piezoelectric nanogenerator and tactile e-skin mechanosensor. Fabricated PNG-15 nanogenerator device showed high electrical output under application of biomechanical energy. Maximum output voltage of ~53 Volt, current density of ~0.3 μA/cm² and instantaneous power density of ~685 W/m³ were achieved from the PNG-15 nanogenerator on the application of 0.3 MPa periodic pressure at 4 Hz frequency. Gentle human finger imparting onto the nanogenerator resulted high output electric power that was used to directly illuminate 85 LEDs. The nanogenerator showed remarkable performance with an efficiency of 13.86%, and can set a pave in self-powered portable and flexible electronics devices. The cost effective, simple nanogenerator may open up a new platform for human body motion based energy harvester converting low-frequency mechanical energy into electricity. Fabricated tactile e-skin was also successfully used to detect pressure stimuli of low limit with high sensitivity in static and dynamic conditions. In dynamic condition self-powered e-skin exhibits high sensitivity (~ 0.97 V/kPa⁻¹) over low to medium pressure region with very short response (~1ms) and relaxation (~2 ms) time. A health-data glove (right hand) attached with e-skin sensors was capable to precisely distinguish the minute motions of three different fingers of human right hand. The sensor was able to sense very low static pressure stimuli in the range of 0.1 kPa to 1.2 kPa with high sensitivity (26.58 MPa⁻¹). It

can successfully sense a minimum weight of 10 mg. A self-powered flexible sensing matrix fabricated by e-skin (pixel) sensors resolved spatial distribution of static pressure and distinguished shape of an object. Results of our work suggest that apart from the applications of the PVDF nanocomposite in nanogenerator for scavenging low intensity biomechanical energy to power personal portable electronic devices, the nanocomposite could be used in the first metal oxide based inorganic-organic e-skin mechanosensor which can be eventually employable in wide range of applications including healthcare monitoring, robotics, and artificial intelligence.

ASSOCIATED CONTENT

Supporting Information

Characterization and measurement techniques, XRD histogram, FESEM micrograph, FTIR results, Zeta potential distribution curve, dielectric properties. DTA-TGA results, DSC heating and cooling curves, surface charge dipole interaction model and mechanism of β phase formation, rectified output voltage of nanogenerator, mechanical property, calculation of energy conversion efficiency, durability testing.

Video VS1: Demonstration of the generation of piezoelectric voltage (rectified) by imparting of human fingers.

Video VS2: Demonstration of the generation of piezoelectric voltage (rectified) due to human toe, heel movement and twisting of wrist.

Video VS3: Demonstration of lighting of commercial LEDs instantly by human finger imparting on PSNG. One panel of blue LEDs (85 numbers) were illuminated. LEDs were connected in series.

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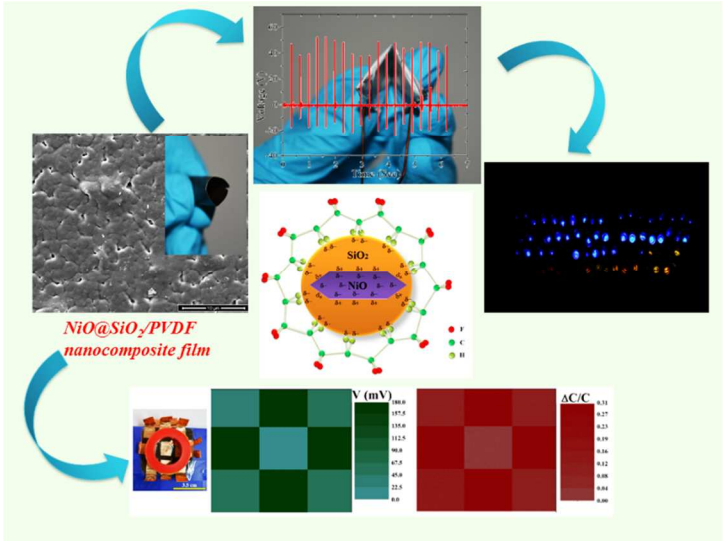
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Table of Contents



Fabrication of flexible piezoelectric energy harvester as cleaner source of alternative energy and e-skin mechanosensor based on PVDF nanocomposite.