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Transparent Sensors

Transparent Piezoelectric Nanogenerator for Self-powered Force Sensing Applications

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Abstract— Piezoelectric materials have been widely used as dynamic force sensors, accelerometers, and energy harvesters. Herein, we report the poly(vinylidene fluoride-co-tetrafluoroethylene) (P(VDF-TrFE)) based transparent piezoelectric nanogenerator (PENG) as a self-powered force sensor. The 2 x 2 array of PENGs was fabricated by sandwiching the P(VDF-TrFE) film between two indium tin oxide-based electrodes. The device demonstrated good stable and repeatable piezoelectric response (sensitivity of 0.3 V N^{-1}), which increased linearly with externally applied compressive force. The output voltage of the devices varied with the frequency of the external force application, and they showed a sensitivity of 0.25 V Hz^{-1} between the 2 to 10 Hz frequency. The excellent dynamic force sensing response, transparency, and self-power feature make presented devices ideally suited for applications such as see-through smart plaster that allow wound healing monitoring without removing the plaster.

Index Terms— Piezoelectric nanogenerators, Transparent electronics, Flexible electronics, Self-Powered sensor, Force sensor.

I. INTRODUCTION

Transparent and flexible electronics is revolutionizing a wide range of applications such as displays, future vehicles, energy generation, e-skins and wearable devices and healthcare technologies [1]. An emerging new technology in this domain is the self-powered sensors based on piezoelectric or triboelectric nanogenerators [2, 3]. These tiny devices use a piezoelectric or triboelectric effect to transform mechanical energy into electrical energy [4, 5]. When manufactured with a high degree of transparency, these devices can offer attractive solutions such as self-powered smart plasters, and smart windows or automobile windscreens etc.[6, 7] The smart plasters with piezoelectric nanogenerators (PENGs) based self-powered pressure sensors could be used to monitor wound healing [8, 9]. Additionally, with transparent PENGs, it is possible to monitor the wound without removing the plaster itself. However, manufacturing an efficient PENG with a high degree of transparency is challenging, as each material layer must exhibit minimal optical absorption while retaining the overall functionality.

Considering this background, herein we report an array of 2 × 2 transparent PENGs, consisting of Indium tin oxide (ITO)-based electrodes and poly (vinylidene fluoride-co-tetrafluoroethylene) (P(VDF-TrFE)) as the active piezoelectric layer. PVDF is a widely used piezoelectric polymer due to its lightweight, ease of processing, good breakdown strength, and the ability to form β-phase that can exhibit good piezoelectricity [10]. Adding TrFE to PVDF facilitates the formation of the β-phase and the growth of favored crystalline orientations, which improves the coupling factor. The fabricated device showed a sensitivity of 0.3 V N^{-1} towards externally applied force (1-10 N), making it suitable for self-powered force or pressure sensing. The devices are also sensitive to the frequency of applied force, with 0.25 V Hz^{-1} sensitivity, that can be utilized to sense vibrations. The transparent PENGs were fabricated using a simple lithography-free method which involved a blade cutter-based patterning technique. The developed devices could be used for smart plaster or touch-based displays. In fact, in the latter case, they could also generate energy when displays are tapped.

II. MATERIALS AND METHODS

A. Materials

Polyethene terephthalate (PET) sheets coated with ITO, having a sheet resistance of 100 Ω/sq. were purchased from Sigma Aldrich and used as electrodes for the PENGs. PiezotechFC30 was purchased from Arkema, having 30 mol% of TrFE and a typical d33 value of -20 pC/N, used as the P(VDF-TrFE). Sensor devices were fabricated by extending electrical contacts from the electrodes using the conductive silver paste, RS PRO (RS 186 – 3600).

B. Device Fabrication

The PENG electrodes were patterned over the ITO-coated PET sheet using a computer-controlled precision cutting machine with a plotter blade (Silhouette Cameo 2) that helps to perform complex patterning without needing expensive lithographic techniques and hazardous chemical etching procedures [11]. For better positioning of the pattern cutting, the ITO-coated PET sheet was attached to a cutting mat. Various parameters, including the blade height, cutting speed, and cutting force were optimized to obtain sharp cuts in the ITO layer, without damaging the PET substrate. P(VDF-TrFE) films were

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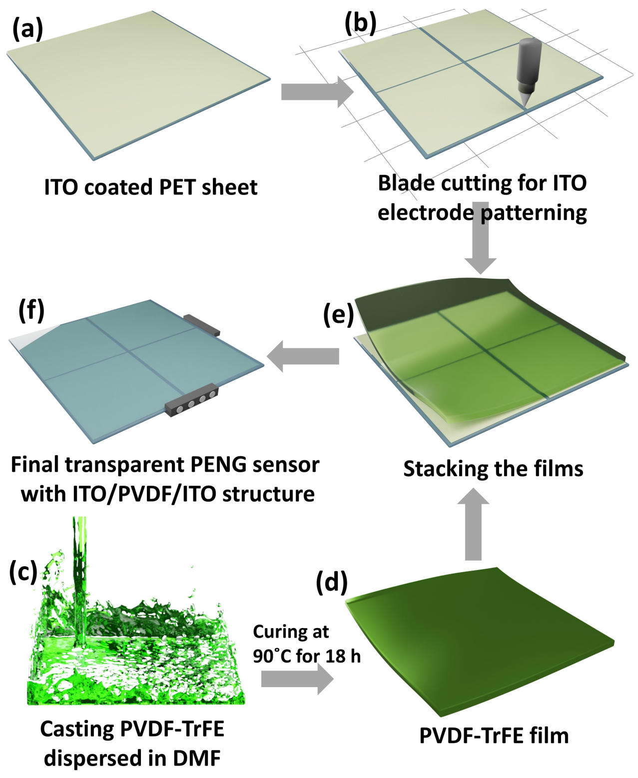

Fig.1. Schematic of the fabrication protocol for transparent PENGs. a) ITO-coated PET sheet. b) Multiple electrodes were patterned using a precision cutting machine. The parameters were optimized to not wholly cut the PET sheet. c) P(VDF-TrFE) dispersed in DMF solvent was cast on a mould to get piezoelectric film, as shown in d). e) The P(VDF-TrFE) active layer was stacked between the patterned ITO-coated PET sheet to complete the device structure. f) Final device after soldering the necessary electrical contacts.

fabricated by the solution casting method. For this, 0.5 g of P(VDF-TrFE) was first dissolved in 5 ml N, N-dimethylformamide (DMF) by constant stirring at 50˚C for 5 hours. This led to P(VDF-TrFE) with 10 wt% concentration. Then the solution was poured into a mould and annealed at 50 ˚C in the oven for 18 hours. The low annealing temperature helps with slow evaporation of solvent that allows the formation of uniform piezoelectric film with good optical transparency. Finally, a homogeneous film was produced by peeling from the mold. Both patterned ITO-coated PET sheets and P(VDF-TrFE) films were stacked as PET/ITO/P(VDF-TrFE) film/ITO/PET to obtain the final device. The electrical contacts were obtained using conducting Ag paste. The complete device fabrication protocol is illustrated in the schematic shown in Fig. 1.

C. Characterization Methods

The active piezoelectric P(VDF-TrFE) layer was characterized using XRD (Miniflex, RIGAKU), FTIR (Jasco FT/IR 4100), and FE-SEM (FEI Nova NanoSem 630). The optical transparency was evaluated using a UV-Vis spectrometer, Shimadzu UV-2600i. The piezoelectric devices were tested using an electrodynamic shaker system (TIRA, TV 50018, Germany) and the output voltage was measured and recorded using an oscilloscope (Keysight MSO-X 4154A). The conditioning circuit consists of a half-wave rectifier developed using IN4001 diodes. An Arduino UNO board was used to convert the generated analogue voltage to digital and to serially communicate the value with the computer for display.

III. RESULTS AND DISCUSSION

A. Material Characterization

The XRD spectra obtained to confirm the phase of the casted polymer film is shown in Fig. 2a. The 2θ peak centered at 19.4˚ represent the presence of both α and β phases [12, 13], while the sharp peaks at 37.8º and 44º indicate the highly preferred orientation in P(VDF-TrFE) [14]. To quantify further, FTIR measurements were performed, peaks (Fig. 2b) at 840, 1076, and 1281 cm^{-1} corresponds to the formation of β-phase. The relative fraction of the β-phase (840 cm^{-1}) compared to that of α-phase (759 cm^{-1}) was calculated as 82.9% [15]. Moreover, the SEM image (Fig. 2c) revealed smooth and homogeneous growth of polymer film of 50 µm thickness. Inset of Fig. 2d shows the finally fabricated device by sandwiching the P(VDF-TrFE) film between two ITO-based electrodes, with BEST placed underneath is clearly visible confirm good optical transparency. The ITO-coated PET exhibited an optical transparency of 91% at 550 nm, while P(VDF-TrFE) showed 64%, which is the limiting factor (Fig. 2d). The overall device was 62% transparent, which can be further improved by optimizing the P(VDF-TrFE) concentration and the active layer film thickness in future.

B. PENG-based Sensor Characterization

The externally applied force induces charge separation inside the P(VDF-TrFE) composite material, and as a result, the voltage is generated between the device electrodes. Along with piezo response, the triboelectrification of the PET substrate will also contribute to the output voltage. The piezoelectric performance of the device, and their

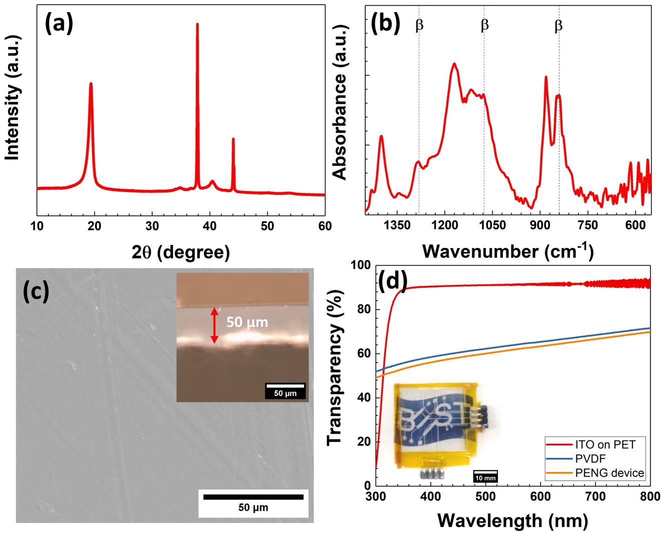

Fig. 2. Material characterization. a) XRD and b) FTIR spectra of the P(VDF-TrFE) confirming the β-phase. c) SEM image of the as-prepared P(VDF-TrFE) film that confirms smooth and uniform growth of the film. Inset shows the cross-sectional image of P(VDF-TrFE) film. The film is 50 µm in thickness. d) The optical transparency of the individual layers and the overall device. Inset shows the final fabricated transparent PENG, with BEST logo underneath the device, confirming the transparency.

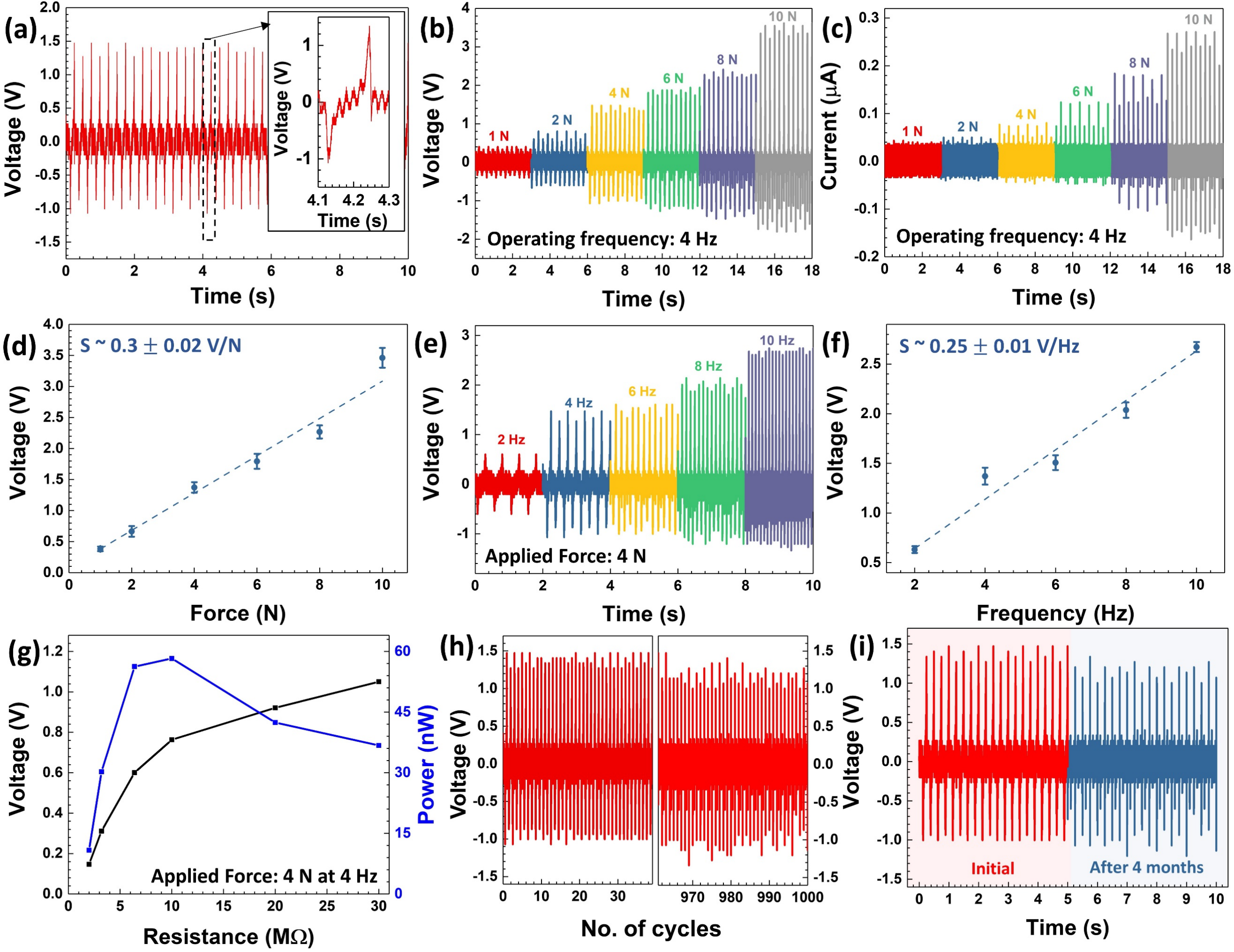

Fig. 3. PENG Characterization. a) Output voltage of PENG for applied force of 4 N at 4 Hz frequency and inset shows the magnified view of the pulses. b) Piezoelectric output voltage and c) current of the sensor for various external applied forces ranging from 1 to 10 N. d) Piezoelectric sensitivity of the device as a function of applied force. e) Piezoelectric output voltages of the sensor at an external force of 4 N applied at various frequencies. f) Piezoelectric sensitivity of the sensor as a function of the frequency of the applied force. g) Variation in the output voltage and corresponding power at 4 N 4 Hz input force for various output resistive loads. The maximum power was observed for 10 MΩ load. h) The output voltage variation as a function of repeated measurement. The device is reliable after 1000 cycles of operation and i) the device's performance is repeatable after 4 months which confirms its stability.

suitability as force sensors, were analyzed by measuring the generated output voltage. Fig. 3a shows the output voltage generated for a repeated compression and release force of 4 N applied at a constant frequency of 4 Hz. A uniform response is observed with periodic positive and negative alternating voltage peaks. Inset shows the enlarged view of the generated voltage signal. The generated signals are stable and repeatable, with a fast response time of < 50 ms. To further quantify the force sensitivity of transparent PENG, four devices were tested for a range of force from 1 to 10 N, the voltage and current responses from the best device are shown in Fig. 3b and c, respectively. Generated output voltage and current were observed to be increasing with applied force and exhibited a sensitivity of 0.3 ± 0.02 V N^{-1}, which has a linear relationship with the externally applied compressive force (Fig. 3d). The device, developed with casting method, exhibits performance on-par with previously reported PVDF-based transparent PENG, as shown in Table 1. In the future, methods such as electrospinning could be used to improve the device's optoelectronic efficiency.

The output voltage of PENGs also depends on the frequency of the external force, which confirms that the voltage generation is highly influenced by the applied strain rate [2]. For a given applied force of 4 N, the PENG generated 0.6 V at 2 Hz frequency while the generated voltage increased to 1.4 V at 4 Hz and 2.7 V at 10 Hz, as shown in Fig. 3e. A linear increase in the response was observed with frequency, at a sensitivity of 0.25 ± 0.01 V Hz^{-1} between the 2 to 10 Hz frequency range (Fig. 3f). Electric charge conservation in the circuit can explain

Table 1. A Comparison of various PVDF-based transparent PENG devices.

Ref.	Active material	Fabrication technique	Performance	Device area (cm^2)	Sensitivity (V N^{-1})	Transparency (%)
[13]	PVDF-HFP	Printing	6.3 V, 250 nA@50 N, 4 Hz	2.5 × 2.5	0.131	55
[15]	P(VDF-TrFE)	Electrospinning	11 V, 1.3μA @10 N, 5 Hz	3 × 1	-	71
[10]	GQDs/PVDF-HFP	Spin coating	6 V, 25 nA @ 10 N, 2 Hz	-	-	-
This work	P(VDF-TrFE)	Casting	3.6 V, 270 nA@ 10 N, 4 Hz	1 × 1	0.3	64

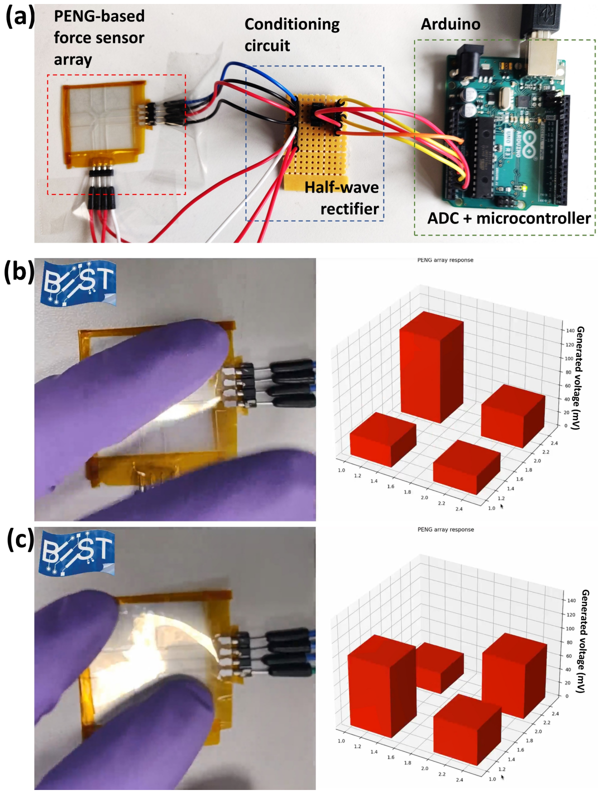

Fig. 4. Array implementation. a) Photograph for reading circuit of the force signal from PENG-based force sensors. Response from the PENG-based 2 × 2 force sensor array for b) single and c) multiple touches.

the frequency-dependent behavior of PENGs. As frequency rises, the tapping period of the PENG-connected circuit shortens, enabling more electrons to flow through each time and raising current and thereby the voltage generated [15]. This frequency-dependent increase in the piezoelectric output could be utilized for measuring mechanical vibrations, accelerations, and orientations [16]. The device delivers maximum output power at 10 MΩ load, as shown in Fig. 3g. A repeatability test was also carried out (Fig. 3h), in which the device was found to be functional even after 1000 cycles of operation and stable after 4 months (Fig. 3i)- thus confirming the durability and stability of the device.

C. Array Implementation

A 2 × 2 array of the PENG-based force sensor was fabricated as mentioned earlier in the fabrication section. Fig. 4a shows the photograph for the readout electronics for the PENG-based dynamic force sensor. PENG is a self-powered sensor that produces the voltage across the terminals when a force is applied, and the generated voltage depends on the magnitude of the applied force. A half-wave rectifier was used to filter the positive signals, and an Arduino converted the signal into digital using its 10-bit ADC and processed the data. The touch response from various locations of the 2 × 2 sensor array was plotted as a 3D bar chart using python to represent the magnitude of the applied force and the location. Fig. 4b, c, show the touch at various locations and the corresponding variation in the output plot.

IV. CONCLUSIONS

In summary, we have fabricated a transparent PENG using P(VDF-TrFE) as the active material and ITO-based electrodes. The fabricated device exhibited stable and repeatable voltage output in response to the externally applied force and showed a linear sensitivity of 0.3 V N^{-1}. The generated output voltage by PENG is highly dependent on the frequency of the external force. A 2 × 2 array of the PENG-based force sensor was also fabricated to demonstrate the feasibility of developed devices for practical applications. They can be used with displays as touch sensors for extracting tactile and spatial information, or energy harvesters (generating energy in response to tapping during touch). These devices could be developed into smart plasters, allowing wound monitoring without removing the plaster. Future studies include the performance enhancement of the P(VDF-TrFE) films by forming composites with graphene, CNT, metal oxides and polymers and utilizing electrospinning.

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