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Nd Doped Zinc Oxide Based Flexible PVDF Polymer Composite for Energy Harvesting and Sensory Application

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ND DOPED ZINC OXIDE BASED FLEXIBLE PVDF POLYMER COMPOSITE FOR ENERGY HARVESTING AND SENSORY APPLICATION

A Thesis

by

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ABSTRACT

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Flexible Piezoelectric devices have garnered a lot of attention for their potential as energy harvesters and transducers. Zinc Oxide particularly has been doped with different metals and has been incorporated in functional polymers in order to produce flexible piezoelectric devices. In this work, a Neodymium doped Zinc Oxide based flexible piezoelectric energy harvester and sensory device has been developed. For that, neodymium doped zinc oxide has been synthesized using wet chemical co-precipitation method and then has been incorporated in Polyvinylidene Difluoride (PVDF) polymer matrix along with Multiwalled Carbon Nanotubes (MWCNT) to produce flexible piezoelectric films. Silver paste was applied on both sides of the piezoelectric film to produce a compact and flexible piezoelectric energy harvesting device. The piezoelectric outputs of the device were tested at variable tapping frequency ranging from 60 BPM to 240 BPM and pressure (10 to 40 psi). The device was also tested with conventional electronics like bridge rectifiers, capacitors, resistors, LEDs to show its potential as an energy harvester. Compared to other modified ZnO-PVDF based unpoled piezoelectric energy harvesters, this device has shown the most open-circuit output voltage. The device produced the highest piezoelectric open-circuit voltage of 75.8 V. It has also shown an optimum power density of 12.55 $\mu w/cm^2$ at 1MΩ load impedance. Energy harvesting capacity was further tested by placing the device between the shoe soles during running and jogging. The device also demonstrated uniform signals when it was attached to a part of the body and a specific motion was repeated. This study endorses the potential of Nd-ZnO/PVDF/MWCNT based piezoelectric energy harvester as the most efficient Piezoelectric Nanogenerator (PENG) which shows superior power generation along with self-powered sensory applications.

DEDICATION

I dedicate my work to my mother, Afroza Begum, and my late father, Rashid Ul Kabir, whose absence I feel every day and hope I am making him proud.

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At first, I would like to express gratitude to my advisor Dr. M jasim Uddin for the continuous help throughout my journey here at UTRGV. Then I would like to thank all of my lab members for their support and coopertion. I would like to thank my partner, Haimanti Majumder, for being always by my side. I would also like to thank my seniors in the lab, especially Abu Musa Abdullah for helping me even with the little things in research. I would like to thank my friends Prince and Prosanto.

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CHAPTER I

BACKGROUND

Piezoelectricity is an energy source that converts harvested mechanical pressure into electrical energy which has been termed as a piezoelectric nanogenerator (PENG)[1]. A piezoelectric nanogenerator does not require the use of an external power source such as a battery or energy storage; it is a unique device that functions through pressure or vibrations from its surroundings[2]. To produce electricity, energy is harvested from mechanical energy such as tapping a finger or bending the surface of the nanogenerator[2].

Piezoelectricity was discovered in 1880 by two French physicists who happen to be brothers: Paul-Jacques Curie and Pierre Curie. They experimented on various crystals such as topaz, tourmaline, zinc blende, boracite, quartz, and calamine[3–6]. The Curie brothers noted that the crystals produced polar electricity through pressure; they called this pyroelectricity. They measured the voltages produced by a unique device, the “quartz piézo-électrique”[5–7]. They published multiple papers explaining their discoveries and predictions. Unfortunately, the Curie brothers only researched piezoelectricity for a limited time. Thus, research on piezoelectricity did not continue for a couple of years, and other people were not interested in piezoelectricity to conduct any research. The use of piezoelectricity started in World War I when Ernest Rutherford and Paul Langevin created a device that sent acoustic waves in seawater to detect other submarines, this lead to the design of the sonar[3,8,9]. In 1919, a professor had created the first

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crystal oscillator control that used an amplifier and a crystal to receive the desired frequency. This discovery was adapted into the second world war to have communication between airplanes and tanks[9]. From 1940 to 1970, Rochelle salt, $BaTiO_3$, and $LiNbO_3$ were discovered to have high ferroelectric dipole properties like the quartz crystal[9]. The first nanogenerator was produced with zinc oxide by Dr. Z. L. Wang in 2006[10,11]. Since then, research papers on piezoelectricity were published at a rapid rate[3].

Technology has come a long way through history to today. Our early ancestors' technology from millions of years ago was different from the technology we know today. They used fire as light and rocks to create tools and weapons for hunting[12]. Technology started to evolve into gun powder, compasses, steamboats, and clocks[12]. In 1879, electricity was introduced to the world[12]. Many people now had access to light with electricity rather than using lamps and candles. Later came steam engines, railways, cameras, telegraphs, and telephones[12]. In the 1900s, radios, airplanes, televisions, spaceflight, computers, and the internet were made[12]. From 2000 to today, artificial intelligence has become one of the tools we use most in our everyday lives[12].

However, with technology advancing over the centuries, consequences followed, affecting Earth's life. Pollution has become a problem for a couple of centuries already, ever since the Industrial Revolution[13]. It is why modern-day society demands for an energy source that can be sustainable for the Earth. Scientists have already created technology that uses renewable energy, i.e., solar energy. Specialized solar panels absorb the sun's radiation and convert them into electricity[14,15]. Wind energy is another example of renewable energy that uses wind turbines.

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Wind turbines use the wind to spin the blades; the mechanical energy collected from the blades converts into electricity[15,16]. Researchers today continue to look for alternate ways to make more renewable energy for future technology.

Researchers have already found different ways to harvest power from the human body, such as electrical, thermal, chemical, and mechanical. Another published study mentions a group that created a thermoelectrical generator that harvests energy from different human body temperatures. The device was designed to be worn around the wrist, similar to a bracelet that will power a wristwatch[17–19].

A piezoelectric nanogenerator's production requires various piezoelectric materials, for instance, a nanocomposite, nanofiller, and a polymer, poly(vinylidene fluoride) (PVDF). PVDF is a semicrystalline polymer with repetitive components of $CH_2 - CF_2$. PVDF film's benefits include flexibility, enabling it to make stress or pressure on its surface. In other cases, PVDF is applied with nanofillers such as Fe_3O_4, a nanofiller with a great source of dielectric properties and magnetic behaviors[20–22]. $BiVO_4$ is another excellent source of a nanofiller with dielectric properties that favors the β-phase[22,23]. Like the nanofillers listed previously, ZnO also enhances the dielectric properties and works well with PVDF[22,24,25].

Different research groups have demonstrated their piezoelectric samples using different materials. One published study mentioned that they used $NaNbO_3$ and reduced graphene oxide (RGO) to synthesize three different PVDF; the first sample was made of PVDF and RGO, the second sample consisted of PVDF and $NaNbO_3$, and the third sample was synthesized from PVDF, RGO, and $NaNbO_3$.

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The results determined that the β-phase was similar in all the samples, but each sample's voltages differed from one another[22]. Another published study discussed about a group that synthesized Fe_3O_4 using iron (III) acetylacetonate and oleic acid.

With the synthesized iron oxide, the group mixed this chemical with PVDF to make PVDF/iron oxide. The sample produced 35 MV/m using a regular amount of force with the tip of a small piece of metal[26]. Polyethylene glycol (PEG) consists of many small particles of the OH^- bond, allowing it to cover more surface area[3]. Furthermore, the use of PEG with PVDF also increased the negative charge output. A research study suggested that ytterbium (III) salt consists of self-polarization properties that allow the PDVF film to have high characteristics of ferroelectricity[2].

The use of nanofillers helps increase the output of electricity of the nanogenerator when applied with stress. Some examples of nanofillers include PEG, carbon-black, and carbon nanotubes, but of course, each nanofiller comes with different outcomes. Carbon-black can distribute electricity from afar, but it only functions in the γ-phase[27–29]. Carbon nanotubes also have excellent dielectric properties, but they are difficult to work with than other nanocomposites[30]. The current experiment's objective is to create a nanogenerator that works best to assist the PVDF in self-polarization; thus, the dipoles will be enhanced and send out a higher electrical charge. The nanogenerator must reach the β-phase to distribute a high dipolar charge. The β-phase is known for having high polarization and zig-zag structure amongst the five crystalline phases (α, β, γ, δ, ε)[31–33]. The nanofiller aims to obtain an organized crystallized structure in the β-phase that will stabilize the piezoelectric characteristics of the PVDF[22].

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In this study, we have synthesized Nd doped ZnO nanorods by wet chemical co-precipitation method. Later, Nd doped ZnO along with MWCNT have been incorporated in PVDF polymer matrix by drop casting method to create a flexible piezoelectric polymer composite film. Silver paste was applied on both sides of the film along with copper strips as extension to create a flexible PENG. The PENG was tested for finger tapping at variable load frequencies showing a maximum output open circuit voltage of 75.8V and 28.8µA of short circuit current at 240 BPM. The device was also successfully integrated with conventional electronics and was able to generate maximum output power of 81µW at a superior power density of 12.55µW/cm^2. Overall, the device shows new horizons for piezoelectric energy harvesting and self-powered sensory applications.

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CHAPTER II

EXPERIMENTAL

Synthesis of Nanorods

The synthesis of Nd doped ZnO nanorods has been done by wet chemical co precipitation method. Equal parts of sodium hydroxide and zinc nitrate hexahydrate solution were mixed and stirred at room temperature for 2 hours. Later the solution was washed several times with distilled water to remove the impurities and the precipitate was later dried in the oven at 80 degrees Celsius for 8 hours and then the dried powders were calcined for 5 hours at 500 degrees Celsius. Figure 1 shows the SEM image of the synthesized Nd doped ZnO nanorods, a cluster of nanorods have been observed here having widths ranging from 20-70nm.

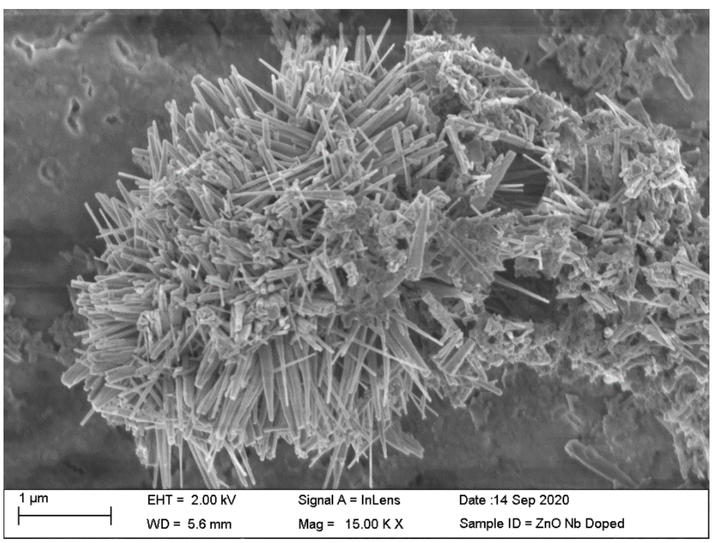

Figure 1. SEM image of zinc oxide nanorods.

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Synthesis of Film and Device Fabrication

The film was synthesized using drop casting method. DMF was used as a solvent. PVDF pellets were added in DMF solution along with Nd doped ZnO and multi walled carbon nanotubes (MWCNT). The solution was then stirred at 60℃ for 24 hours. The solution was then drop casted onto a glass substrate and dried at 60℃ for 24 hours to evaporate any remaining solvent and obtain the flexible piezoelectric polymer composite film. Later the film was cut into a 1 in^2 film and silver paste was added on both sides of the film to create the flexible PENG. Copper tape strips were added at the edge of each side of electrode for electrical measurements. Figure 2 shows the packing design along with the overall PENG structure where the PVDF polymer matrix contains Nd-ZnO and MWCNT and the polymer composite is sandwiched between two layers of silver paste working as electrodes making a compact and flexible structure.

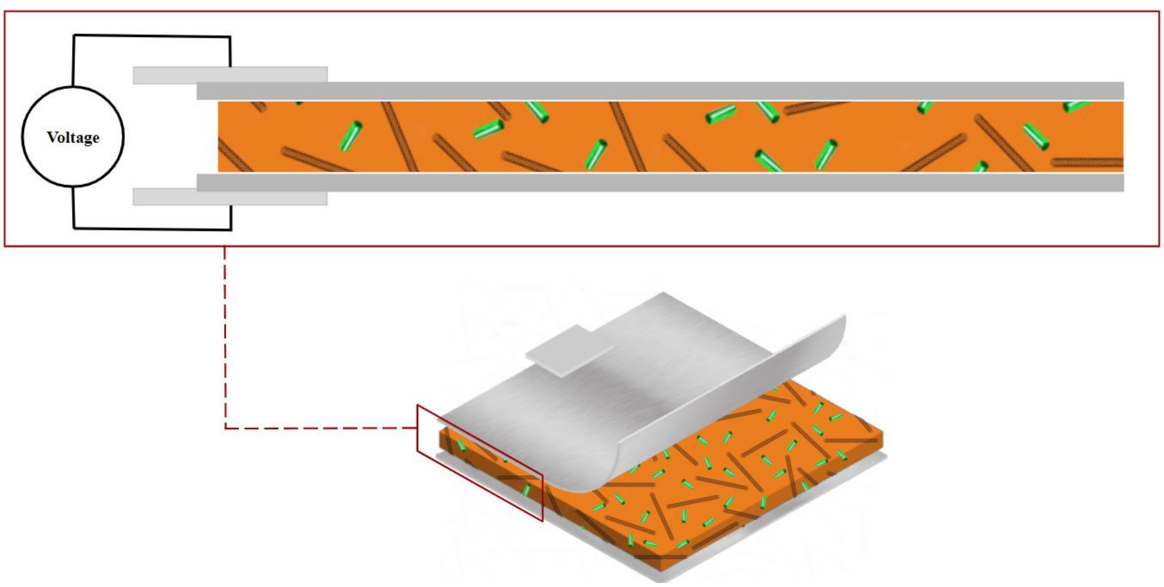

Figure 2. Device structure.

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Characterization

Figure 3 shows the overall the X-ray diffraction peaks for the synthesized pure ZnO along with the Nd-ZnO and it also shows the comparison of the peaks indicating how Nd has influenced the ZnO crystal structure. The XRD peaks for both samples correspond to the wurtzite phase of ZnO and sharp peaks obtained indicate high crystallinity in both samples. No peaks of impurities for Zn, Nd or Nd_2O_3 have been observed. The XRD peaks for Nd-ZnO have shifted towards lower 2 theta values suggesting successful doping of Nd^{3+} ions in the ZnO crystal lattice[34]. Intensification of (101) peak compared to the others in Nd-ZnO conforms to nanorod formation. The peak shifts in Nd-ZnO crystal structure are due to the mismatch of ionic radii of Zn^{2+} and Nd^{3+} ions which results in an internal stress in the crystal structure[35].

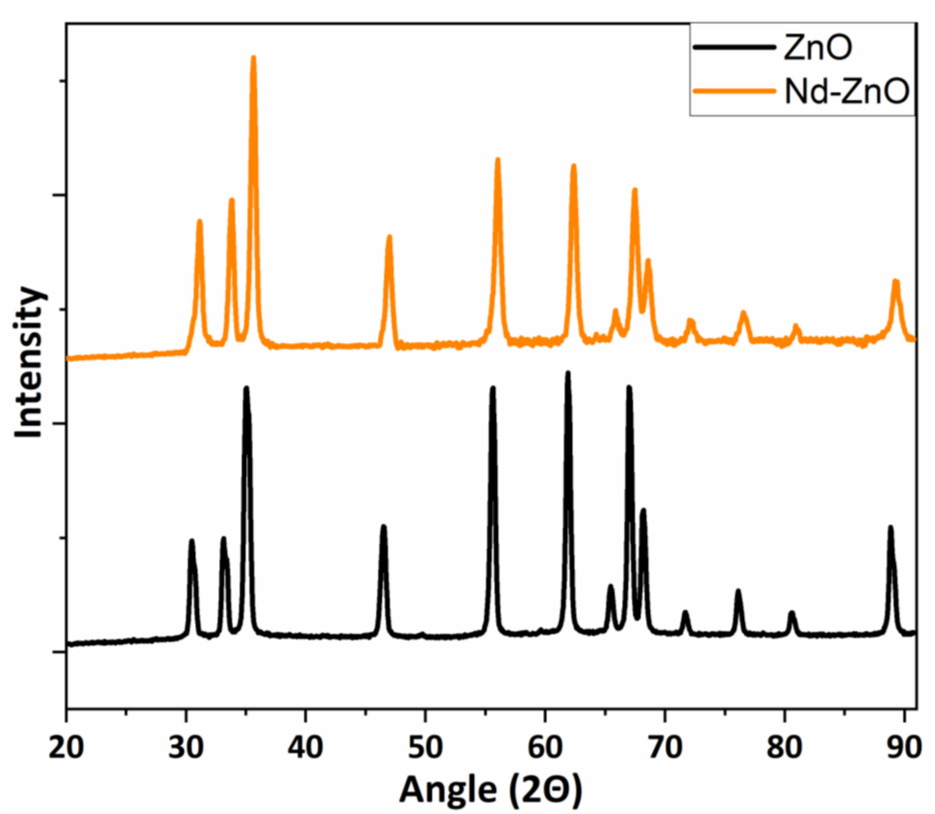

Figure 3. XRD analysis.

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FTIR spectra of the PVDF, MWCNT, Nd-ZnO composite film is shown in Figure 4b. All the characteristic peaks of PVDF are present; sharp peaks at 877 cm^{-1} and 1401 cm^{-1} correspond to the C-F stretching and C-H bending vibrations of PVDF[36,37]. Sharp and strong peaks at 1232cm^{-1}, 833cm^{-1}, 811cm^{-1}, and 481cm^{-1} strongly correspond to γ phase formation[38–40]. Exclusive peaks for β phase are observed at 510cm^{-1} and 1071cm^{-1} wavenumber[36,41,42]. The characteristic peaks indicate that the PVDF is dominant in γ phase along with the presence of β phase. These two phases are the most desirable for piezoelectric properties as β phase yields the highest piezoelectric coefficient in PVDF and γ phase imparts stability at higher temperatures which plugs the reduction of polarization with time[43–45]. SEM image of the PVDF, MWCNT, Nd-ZnO composite film (Figure 4c) shows the surface morphology. Development of a microporous structure can be observed throughout the film. The SEM image shows a uniform microporous structure that aids in enhancing the piezoelectric output[46]. Furthermore, Nd-ZnO nanoparticles were not observed in the SEM images indicating a good dispersion and insertion of the nanoparticles in the PVDF polymer matrix.

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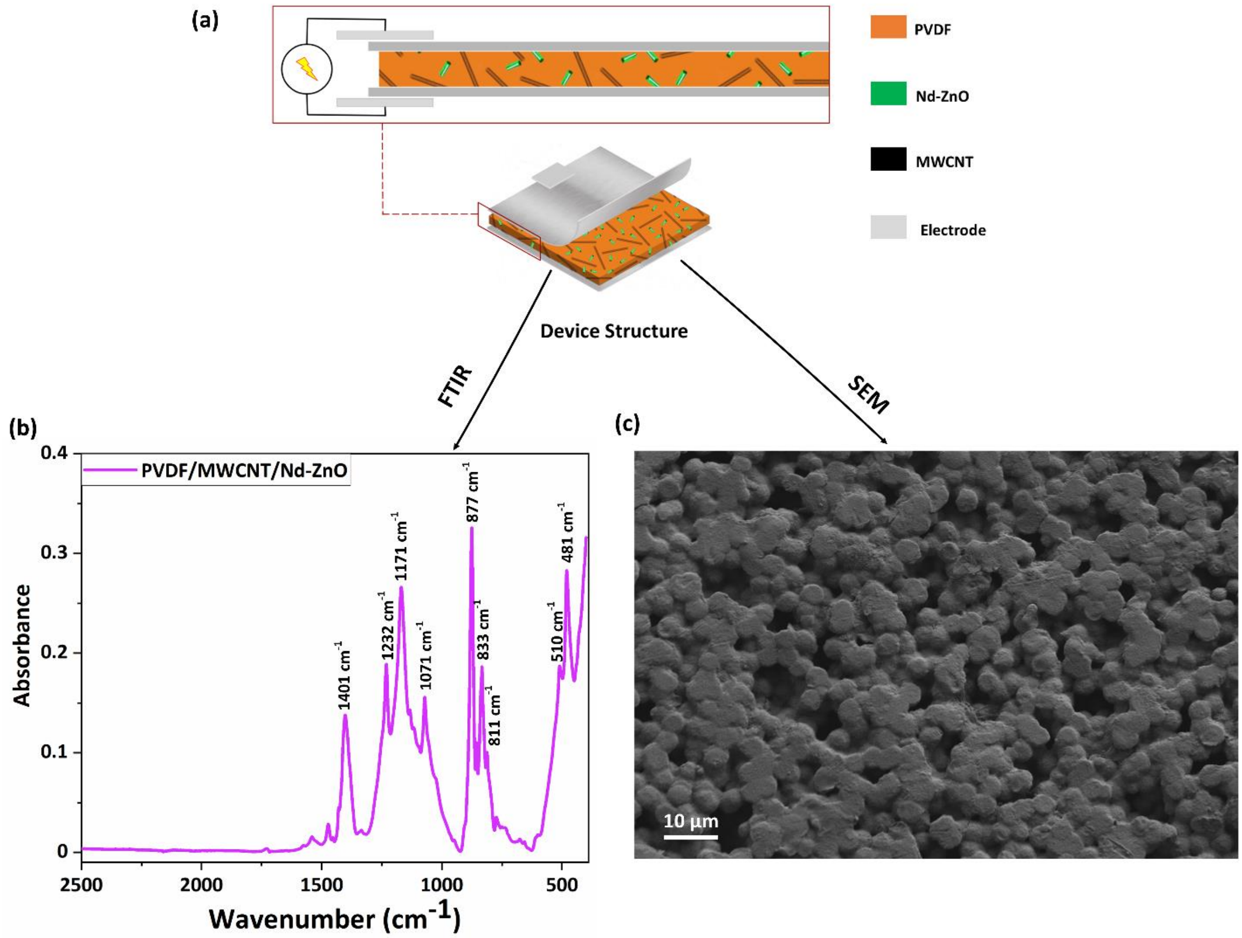

Figure 4. (a) Schematic of PENG structure, (b) FTIR spectra of PVDF, MWCNT, Nd-ZnO composite, (c) SEM image of PVDF, MWCNT, Nd-ZnO composite film.

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CHAPTER III

RESULTS AND DISCUSSION

Electrical Output Analysis and Mechanism

Mechanism of the PENG (Figure 5a) can be explained by the stress induced poling effect[47,48]. When an external force is applied onto the PENG, crystal structures of Nd-ZnO and PVDF get oriented to create electric dipoles. As a result, electrons travel from the upper to the lower electrode when an external force is applied onto the PENG giving a positive voltage signal[47,49]. And when the force is removed, the electrons move in the opposite direction resulting in a negative voltage peak[50]. The positive peaks are higher than the negative peaks as the positive ones are caused by the deformation due to the external force and the negative ones are caused by the PENG trying to regain its original structure[51].

Electric output of the PENG was tested by finger tapping on the PENG surface where the tapping distance was kept at 2 inches between the finger and PENG. Tapping at varying frequencies was conducted and the open circuit voltage (Figure 5b) and short circuit current (Figure 5c) was recorded. Maximum output voltages of 15.4V, 42.4V, 61.1V, 75.8V and currents of 9.6µA, 17.2µA, 24.2µA, 28.8µA were recorded for 60, 120, 180, and 240 BPM respectively with the highest output being observed at 240 BPM. As the tapping frequency increases, the applied force along with the acceleration of impact increases which results in higher piezoelectric output[52].

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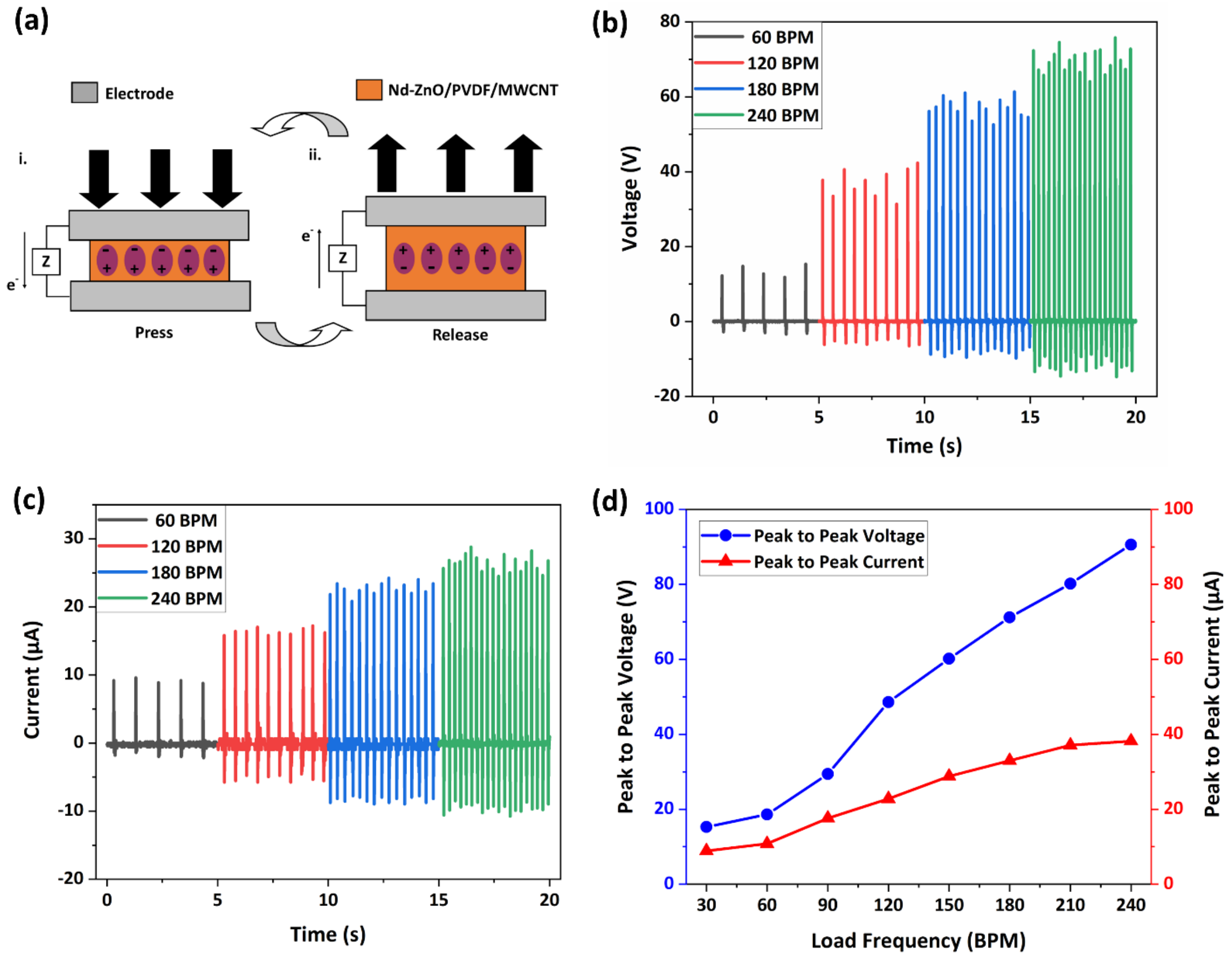

Figure 5. (a) Schematic of the PENG mechanism during i. pressing, ii. releasing, output (b) voltage and (c) current generated by the PENG due to external load at 60 BPM, 120 BPM, 180 BPM, and 240 BPM frequency, (d) maximum peak to peak voltage and current generated by the PENG at different load frequencies.

Higher tapping frequency also leaves the electrons with less time to neutralize and thus enabling the PENG to reach higher current outputs[53]. Figure 5d shows the maximum peak to peak voltage and current generated by the PENG in 30 to 240 BPM tapping frequency range. The output voltage and current showed small change with the change of frequency in lower BPM and then showed a linear increase with the voltage showing a steeper trend compared to the

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current output with the maximum peak to peak voltage and current having the value of 90.6V and 38.2 μA respectively. This can be attributed to the change in the dimension of the PENG due to the deformation caused by the external load; and since resistance varies with deformation, the resistance of the PENG increases with the tapping frequency increase[54–56].

The PENG's ability to harvest and store energy was further tested by creating a circuit (Figure 6a) with a full wave bridge rectifier and then connecting with capacitors, resistors, and LEDs with the circuit diagram for the LEDs shown in Figure 6f. Figure 6b shows voltage output when PENG was charging 0.1μF, 1μF, and 3.3μF capacitors at 180 BPM for 30s with 0.1μF reaching an output voltage of 10.1V in 30s, the latter two showed output of 2.7V and 1.1V respectively during 30s of charging. The highest output voltage was observed for the lowest capacitance, this is consistent with the fact that charge loss is increased with the increase in capacitance[55]. Figure 6c shows the charging and discharging pattern of the 0.1μF capacitor at 180 BPM. Charging is dependent on the external force applied on the PENG, but discharging occurs at a constant rate as there is no load applied during discharging and it is dependent on the capacitor[55,57]. Moreover, the PENG was tested with resistances ranging from 10^5 to $10^8 \Omega$. Average voltage and current outputs were measured for varying resistance (Figure 4d) and the optimum resistance was found at $10^6 \Omega$ where the output power is the highest; this has been corroborated by the peak power curve (Figure 6e) showing maximum power output of 81μW giving the PENG a superior power density of 12.55μW/cm^2. The PENG was able to light 15 LEDs (Figure 6g) with the force generated by 30s of tapping at 180 BPM further exhibiting the PENG's potential to harvest and convert energy.

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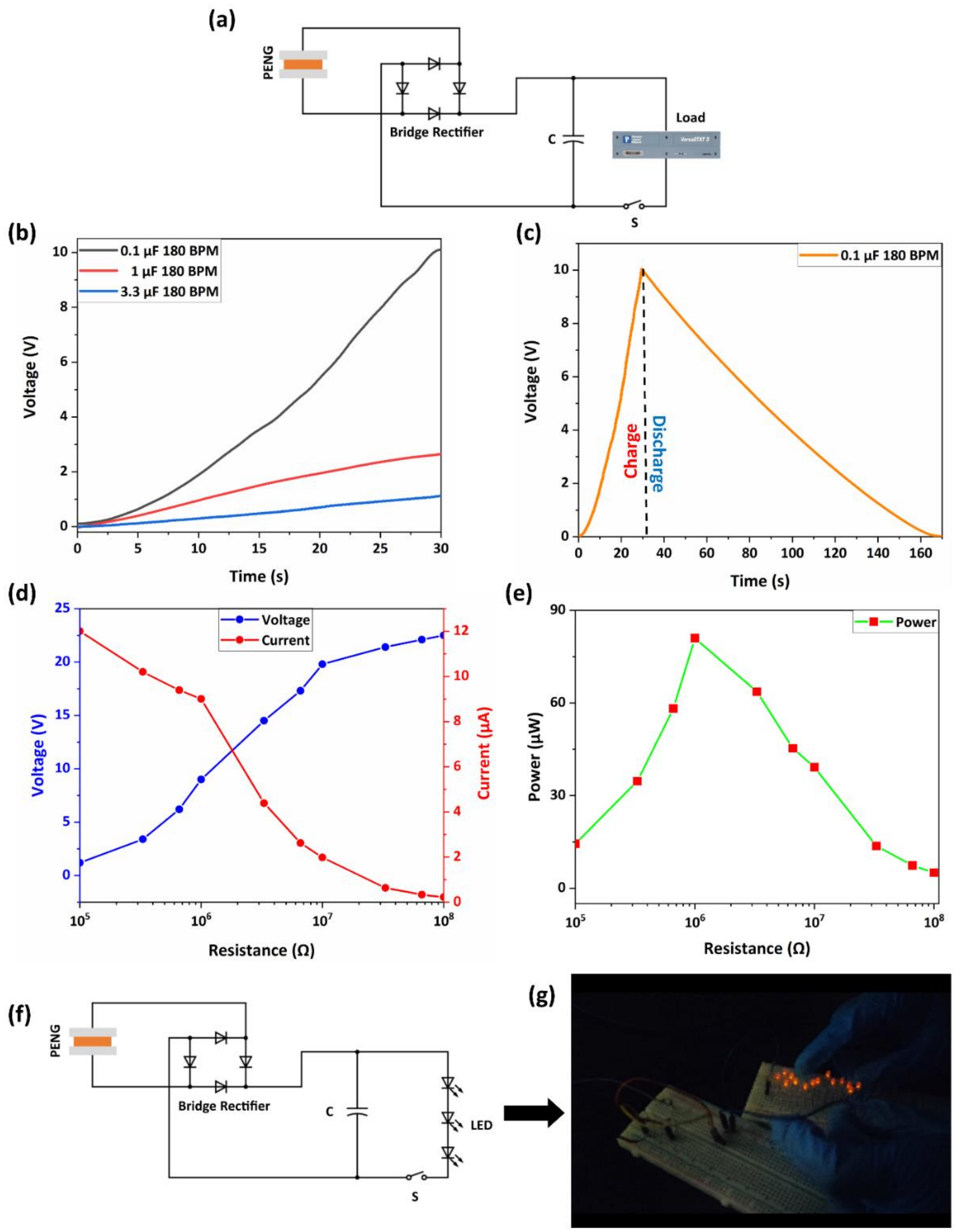

Figure 6. (a) Circuit diagram when PENG is connected to a full wave bridge rectifier, capacitor, and a potentiostat, (b) charging different capacitors for 30s at 180 BPM, (c) charging and discharging of 0.1µF capacitor, (d) average voltage and current with respect to resistance, (e) average power with respect to resistance, (f) circuit diagram when PENG is connected to LEDs with rectifier and capacitor, (g) Lighting of LEDs with PENG.

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Besides energy harvesting, the prospect of the PENG being a self-powered sensor was also observed. For that, the PENG was subjected to constant loads generating by a pneumatic piston of 2cm diameter (Figure 7a). Here, the PENG shows a uniform response while being subjected to a specific load. This suggests that the PENG can be used as a self-powered pressure and force sensor. To further test the PENG's sensory ability, it was attached to the forearm and fist opening and closing motion was repeated at 60 BPM (Figure 7b) demonstrating that the PENG generates uniform and specific signals for this type of movement. To further test the charging power of the PENG, it was placed between the two soles of a shoe and static jogging and running motion were conducted at 120 BPM and 240 BPM while wearing the shoe and the PENG's charging capacity was recorded for 0.47μF and 1μF capacitors. The PENG was able to reach 7.6V and 11.1V in 20s with the 0.47μF capacitor while jogging and running respectively. And for the 1μF capacitor the PENG reached 2.4V and 4.7V in 20s for jogging and running respectively. As the PENG's force sensing was already established in Figure 7a, this further proves that the PENG can be utilized for biomechanical motion tracking by sensing the force generated by the footsteps and powering itself while doing so. The PENG's bending deformation response was also tested by attaching it on the outside of elbow. Figure 7d demonstrates the signal generated by the PENG when it is subjected to bending of elbow from straight position to 90 degrees at 60 and 90 BPM frequencies. The response at both frequencies shows the same characteristic peaks for elbow bending with higher voltage generated at higher frequency suggesting the PENG can detect the movement along with the intensity of the movement. These tests clearly suggest that the PENG has the potential to be utilized as a self-powered pressure, force, and biomechanical motion sensor.

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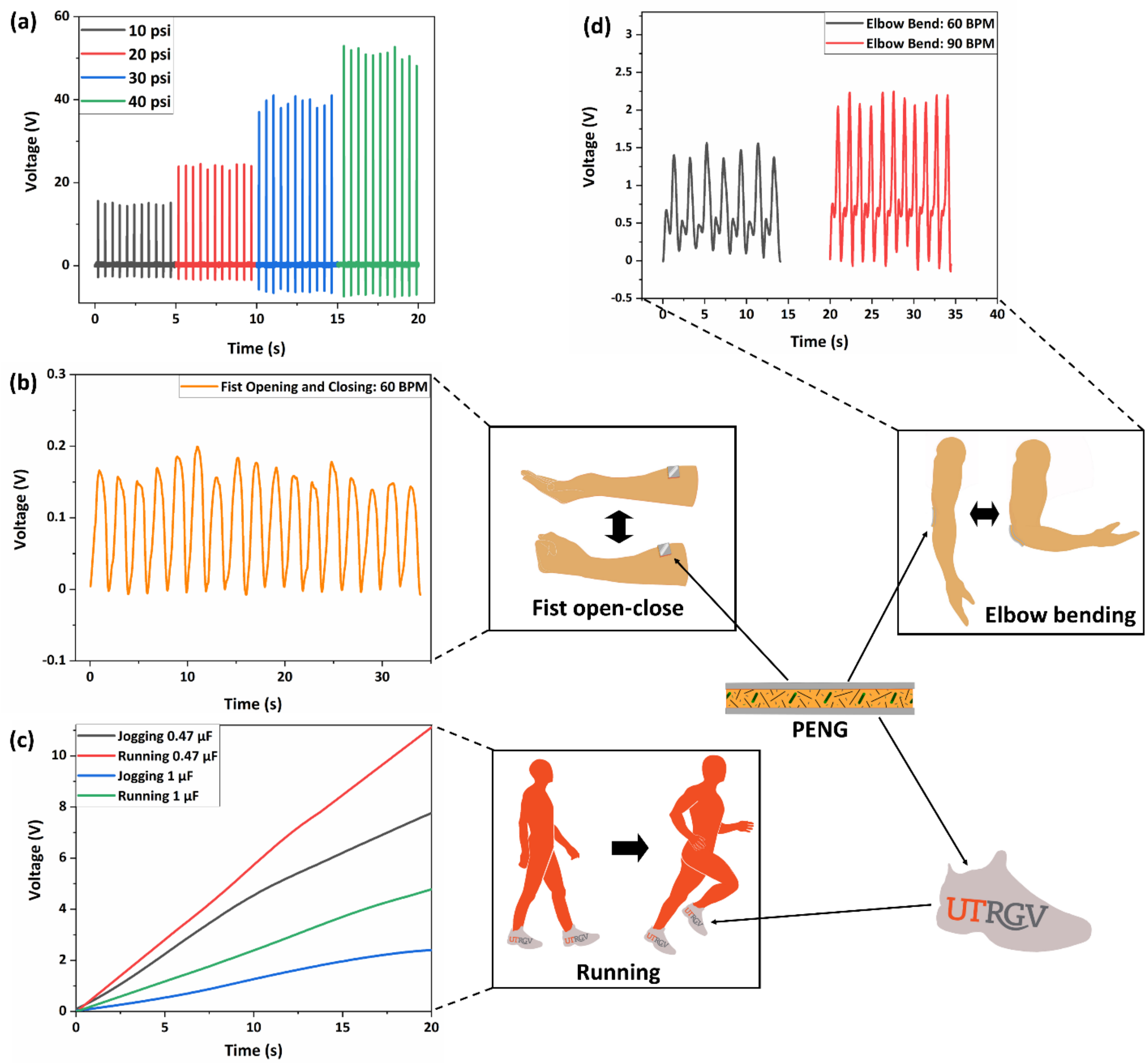

Figure 7. Response of PENG with (a) changing pressure, (b) fist opening and closing when attached to forearm at 60 BPM, (c) jogging and running while PENG is inserted in shoe, (d) bending of elbow at varying frequencies.

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CHAPTER IV

CONCLUSION

In this work, we have successfully incorporated Nd doped ZnO in PVDF polymer matrix along with MWCNT to create a simple yet superior piezoelectric energy harvesting device. The PENG was able to generate a maximum output open circuit voltage of 75.8V and 28.8µA of short circuit current under finger tapping at 240 BPM. The device was also successfully integrated with conventional electronics and was able to generate maximum output power of 81µW at a superior power density of 12.55µW/cm^2 giving the PENG a higher power density than some of the more complex piezo-triboelectric hybrid devices making this a simple yet efficient solution in piezoelectric energy harvesting[55,58]. The device was also successfully tested for self-powered force and biomechanical motion sensing and paving the way for cheaper and easy to produce sensors. Because of the low energy need during the whole fabrication process from the nanorod to composite film synthesis, this simple yet unique structure shows new horizon in the ZnO based nanogenerators and their impact in energy harvesting and self-powered sensory applications.

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BIOGRAPHICAL SKETCH

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