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Piezoelectric Energy Generation and Harvesting at the Nano-Scale: Materials and Devices

Review Article

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Abstract Continuous efforts are being made for alternative power generation techniques for use in devices with sub-micron-scale dimensions. In this work, we have perused through some of these efforts, focusing mainly on devices using materials with piezoelectric properties. In the last decade or so, nanostructured zinc oxide (ZnO) has drawn worldwide attention for its path-breaking properties. One of its most extensively-studied properties is its ability to generate power when subjected to mechanical vibration. It can generate a potential within a wide range of frequency vibrations, from a few Hz to thousands of KHz. This can lead to extensive application prospects in many important fields, like self-power generating devices for medical applications, wireless technologies and various sensors, etc. This review looks into reports related to such technology in detail. It also takes into account certain other materials that have been reported for piezoelectric energy scavenging applications.

Keywords Piezoelectricity, Nano-Generator, ZnO, Lead Zirconium Titanate (PZT), Polyvinylidene Fluoride (PVDF)

1. Introduction

Piezoelectric energy harvesters at the sub-micron-scale have infinite scope for research and application in upcoming technologies [1]. Devices for wireless technologies [2] and medical applications for replacing vital human organs need to be small and are required to be powered for their functioning as active devices [3]. Recent embedded electronic devices like RFID tags and remote sensors are giving stand alone and MEMS/NEMS devices a new dimension [4]. These devices, despite consuming very little power, require separate energy sources. The self-powering of these devices has remained an issue and is a new field of research in state-of-the-art technologies [5]. In this review, we look into energy harvesting materials and devices for micro-/nano-electromechanical systems, which can be made much smaller and lighter than conventional sources [6, 7].

The use of the piezoelectric properties of certain materials is a very promising source of alternative energy harvesting methods [8,9]. Piezoelectricity is a natural property of certain materials to generate electric potential

when they are subjected to mechanical stress [10, 11]. We look into the metal oxide semiconductor nanostructures of ZnO that can be cost effectively fabricated for their piezoelectric properties and their use in building energy harvesters [12, 13].

Materials with a high dielectric constant and an inherent directional quality can be made to produce surface charges or electrical polarization by applying mechanical stress. Single crystal materials demonstrate a piezoelectric character similar to that shown by perfectly-aligned polycrystalline ceramic elements [10]. We explore those piezoelectric nanostructures that can be used to transform mechanical vibrations into electrical energy and for self-powering micro-/nanosystems, like micro-sensors for medical diagnostic applications and drug delivery systems for *in vivo* therapeutic applications [14]. The human body produces mechanical energy through various sources, like the heartbeat and blood flow, which can be used for self-powered implantable micro-/nanosystems. We extensively examine here how zinc oxide and other piezoelectric ceramic and polymer nano- and micro-structures have been used over the last few years for such applications [15].

The first ever source for electrical power was invented by Alessandro Volta in 1799 and was known as a battery [16]. After the invention of the generator by Michael Faraday in 1831, the lighting up of cities through a wiring process came into existence, while batteries became the major power source for wireless electrical devices. These batteries had huge sizes and weighed an enormous amount too. The wireless radios of the early 1900s, using vacuum transistors and batteries, were heavy [17]. With the fast evolution of large-scale integration (LSI) techniques, electronic devices are continuously shrinking in size. As a result, electronics has approached the nanotechnology domain. With the unprecedented decrease in electronic device sizes, ever greater numbers of transistors (a few billions) are being integrated into single ICs using very large-scale integration (VLSI) techniques, and complex functions are being performed [18]. With the interfacing of hardware and software through HDL languages and embedded systems, electronic systems have forayed into practically all fields of science and technology. However, each and every device needs to be powered for its operation [19]. Conventional batteries have been significantly reduced in size and cost by the use of newer technologies. However, all batteries need to be changed and/or recharged frequently. Also, due to the use of hazardous materials in their fabrication, they are very difficult to dispose off without affecting the environment [20]. These limitations have restricted their application in the fields of medical diagnostics and *in vivo* treatments. We explore the newest devices for self-powered systems - like various micro-sensors for different sensing applications [21], medical diagnostic applications and drug delivery systems for *in vivo* therapeutic applications - using piezoelectric energy harvesting methods that could lead to an increase in human life expectations and longevity [22]. We investigate whether autonomous micro-/nanosystems harvesting energy from the environment could become a reality [26].

Naturally abundant kinetic energy available in the form of different environmental, man-made and mechanical vibrations or motions can be used for piezoelectric energy scavenging [23]. Piezoelectric energy scavengers are found to be very simple, with comparatively higher energy conversion rates. Mechanical vibrations are available in plenty from footsteps on floors to car engine vibrations with a multiplicity of frequencies. The human body produces mechanical energy through various motions like bodily gestures, heartbeats and blood flow, etc. [24]. The concept of wireless systems with a long battery life led to the development of MEMS-based vibration energy harvesters otherwise known as micro-generators [25]. We look into the various materials used for such devices, which have mostly been ceramics or polymer piezoelectric materials like PZT or PVDF. Energy generation was usually done by binding them to vibrating structures to gain physical strain for the generation of electrical power [26]. Some devices even used human movement for energy generation. These microsystems have larger structures, usually within the range of a few cubic centimetres and could have operating frequencies within the range of 50 Hz to 5 KHz [27, 28]. Hence, these structures are handicapped by their larger size and limited operational frequency range. In addition, they are severely dependent on the resonance frequency for the proper functioning of the device. Vibration-based micro-generators have been shown to be capable of providing a power output of up to 4 $\mu W/cm^3$ when stimulated by very low frequencies, like human motion, and up to 800 $\mu W/cm^3$ when stimulated by machine motions at high frequencies [29]. In this review, we investigate how the nanostructures of these piezo-generating materials have an edge over MEMS-based energy scavengers, including their operating principles, the problems associated with them and the possibilities of overcoming them.

We look into the piezoelectric energy generation properties of a semi-conducting crystal, ZnO [30], and how it can be used to convert biological mechanical energy, acoustic or ultrasonic vibration energy and bio-fluidic hydraulic energy for self-powered wireless nano-devices and systems [31]. We study the various properties of ZnO, such as band gap and Young's modulus of elasticity of one-dimensional nanostructures, and how these make it a superior material for piezoelectric energy

harvesting [32]. We also explore other materials that are good for building such energy harvesters and make a Comparison among these materials.

We note how a single nanowire can work as a nano-transducer and generate piezoelectricity. We explore the integration of multiples of these nanowires into arrays on a single substrate for improved output power. We also gain an insight into the use of polymers and ceramics for the same. In a nutshell, in this review, we look into the key issues for harvesting piezoelectric energy and how nanostructures could be fabricated and assembled to work as a self-powered nano/micro-structured device.

2. Piezoelectricity

Piezoelectricity, an innate attribute of ceramic materials, was discovered by Pierre and Jacques Curie in the year 1880 [33]. Piezoelectricity can be defined as the property of certain materials to produce electrical potential when subjected to mechanical stress. Some natural piezoelectric materials include DNA, enamel, silk, dentin, etc. [34]. Single crystals, like quartz, ZnO and synthetic crystalline materials, and ceramics like barium titanate, lead titanate, lead zirconate titanate, sodium potassium niobate, bismuth titanate, etc., and polymers like polyvinylidene fluoride, are found to exhibit this property [35]. Electrically-charged particles in substances are distributed in space in such a way that the opposed charges cancel each other out. This makes matter electrically-balanced so that they do not have excess electrical charge and are, hence, neutral. When mechanical strain is produced in the form of a physical deformation, certain materials undergo a forced-charge unbalance at their surfaces, which we term 'piezoelectricity'. Surface charge separation can occur, depending on certain attributes of the material [36]. These include the dielectric capacity and crystal structure of the material or, in other words, how it is aligned with respect to the central axis of the crystal [37]. Certain materials possessing high dielectric capacities and inherent asymmetric orientation about their axis can be made to produce a separation of surface charges under applied mechanical stress. Piezoelectricity is exhibited by polycrystalline materials of ceramic type with a perfect orientation, as well as a few single crystal materials. Ceramics like PZT, on the other hand, are mixtures of minute piezoelectric crystallites randomly-oriented. Hence, piezoelectric behaviour usually cancels out at the macro-level. The permanent alignment of these crystallites is to be achieved through the application of external electric fields for piezoelectric properties at the macro-level [36].

The piezoelectricity of any material is measured by its piezoelectric coefficient or piezoelectric modulus (D). 'D' can be defined as the change in volume that it undergoes when subjected to an electric field or as the polarization that it undergoes when mechanical stress is applied. This is mathematically represented as $D = P/\sigma$, with 'P' denoting the polarization and 'σ' the stress. There can be many piezoelectric coefficients, depending on the crystal orientation [38].

2.1 Piezoelectricity in ZnO

Zinc oxide, a II-VI metal oxide semiconductor material, is known for its versatility. ZnO nanostructures exhibit anisotropic piezoelectric properties due to its structural non-central symmetry [39, 40]. High aspect ratio ZnO nanostructures can be easily synthesized using hydrothermal methods [41], and these nanowires or nanorods exhibit piezoelectric properties (i.e., they produce electrical energy when supplied with mechanical stress [42]).

In single crystal solids like ZnO, the piezoelectric property of the material originates with its atoms and is repeated throughout the solid due to high crystallinity. The non-symmetric distribution of positive and negative charges starts at a unit cell and repeats through the whole material. A strained material results in net polarization on the surface.

Crystal Structure	Hexagonal Wurtzite
Piezoelectric Coefficient	**12 pC/N**
Molecular Weight	81.38
Lattice Constants (300K)	a = 0.32469 A°, c = 0.52069 A°
Melting Point	2248 K
Density	5.606 g/cm^3
Thermal Conductivity	25 W/mK at 20°C
Fusion Heat	4,470 cal/mole
Band Gap	3.37 eV at room temperature
Thermal Expansion Coefficient	4.3x10^{-6}/°K at 20°C and 7.7x10^{-6}/°K at 600°C
Refractive Index	2.008
Lattice Energy	964 kcal/mole
Exciton Binding Energy	60 meV
Electron and Hole Effective Mass	m_e * = 0.24 eV, m_h * = 0.59
Dielectric Constant	ε_0 = 8.75, ε_∞ = 3.75
Intrinsic Carrier Concentration	< 10^6 cm^{-3}
Electron and Hole Mobility (300K)	μ_e = 200 cm^2/(V.s), μ_h = 5-50 cm^2/(V.s)

Table 1. Important material properties of ZnO [44].

ZnO nanostructures are very versatile, like their bulk counterparts, and can endure huge deformations [43].

This characteristic attribute of the semiconducting piezoelectricity of ZnO nanorods/nanowires is being studied intently for the creation of novel devices. This is paving the way for size-attuned sources of power for wireless devices which have themselves been undergoing a continuous size reduction over the years [44, 45]. A few of the important material properties of ZnO are given in Table 1.

2.2 Principle of piezoelectric generation in ZnO nanowires

If a straight vertical nanowire is deflected, a strain field is created as the outer surface is stretched and the inner surface is compressed, resulting in an electric field along the z direction of the nanowire. This is given by $E_z = \varepsilon_z/d$, where 'd' is the piezoelectric coefficient along the nanowire. The piezoelectric field is parallel to the z-axis at the outer surface and anti-parallel at the inner surface. At the tip, the electric potential varies approximately from V_s^- at the compressed side to V_s^+ at the stretched side. The relative displacement of the Zn^{2+} ions with respect to O^{2-} ions creates a potential difference, which can recombine only after releasing the strain. Hence, the potential difference remains so long as the deformation remains and the strain field increases with the amount of bending [48]. Figure 1 shows the variation of longitudinal strain field, electric field and generated voltage across the length of a ZnO nanorod when subjected to deformation.

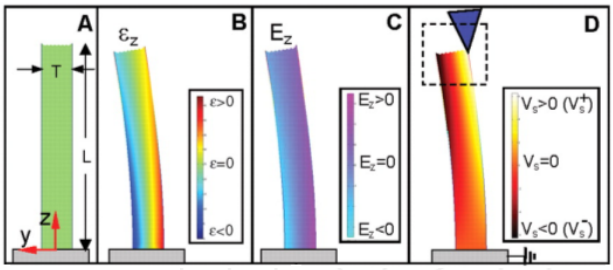

Figure 1. Principle of power generation in a ZnO NW: (A) Schematic of the NW and coordinate system. (B) Longitudinal strain ε_z distribution in the NW after deflection by an AFM tip from the side. Image shows a FEMLAB simulation for a ZnO NW of length 1 μm and an aspect ratio of 10. (C) Corresponding longitudinal electric field Ez distribution in the NW induced by the piezoelectric effect. (D) Potential distribution in the NW [48].

If an external resistance is connected as a load during the contact mode scanning of aligned ZnO nanowires while maintaining a constant force between the sample and a metal-coated AFM tip, an output voltage can be measured as observing sharp voltage peaks due to the generated piezo potential [49].

3. Properties of ZnO nanostructures

ZnO is highly piezoelectric [50] and has been found to have the largest piezoelectric coefficient among tetrahedral crystals, giving very high electro-mechanical coupling [51]. ZnO nanostructures are also piezoelectric [52], having high elasticity, and hence can be bent to a large extent [53]. The piezoelectric coefficient is much higher for nanostructures as compared to their bulk wurtzite structure. It has been found to be much higher for low frequencies as compared to high frequency vibration. This was proven by piezo-response force microscopy done using an AFM tip on a ZnO nanobelt surface by Zhao et al. [54] Figure 2(a) shows the piezoelectric effect on the tetrahedral coordination of Zn^{2+} cations and O^{2-} anions of a ZnO crystal. As shown, a cation is surrounded tetrahedrally by four anions and the negative charges are centred at the tetrahedron centre coinciding with the location of the positive charge. When under mechanical strain, the centre of gravity of the negative ions gets distorted, shifting position and thereby creating an electric dipole. If all such tetrahedrons have the same orientation, or such an orientation where the mutual cancellation of opposite charges is not allowed, the electric charge separation will be multiplied at the macroscopic level. This will give us two opposite charges accumulating at two different faces of the deformed macrostructure.

Figure 2(b) shows the piezoelectric coefficient of ZnO nanobelts measured experimentally and its comparison with that of bulk ZnO. Depending on the frequency, the effective piezoelectric constant was found to vary between 14.3 pm/V^{-1} and 26.7 pm/V^{-1}, which is far greater than the bulk value of 9.93 pm/V^{-1} [55].

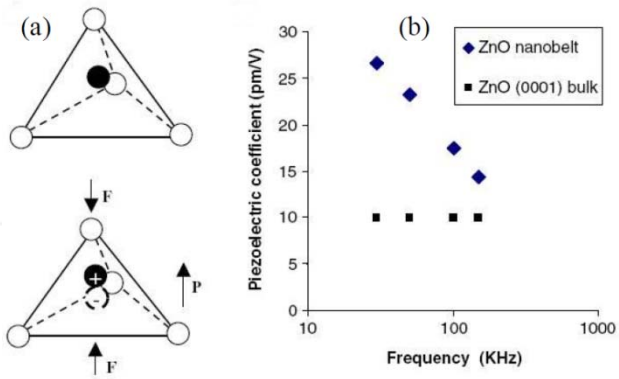

Figure 2. (a) Effect of piezoelectricity on the tetrahedral coordination of a ZnO crystal and (b) change in piezoelectric coefficient with frequency [54].

ZnO thin films have high piezoelectric coefficient values of 7-8.5 pC/N [56]. For nanowires within an optimum diameter range of 45 nms to 33 nms, Young's modulus of elasticity increases with a decrease in the diameter due to an increased surface-to-volume ratio [57]. For wires that are too thin or too thick, it becomes comparable to that of the bulk values [58]. The presence of defect states results in lower electromechanical coupling in the nanowires beyond this range, resulting in lower piezoelectric coefficients [59]. Along with Young's modulus, the electronic band gap of ZnO nanowires is also increased as compared to their bulk values, due to quantum confinement. This makes the

thinner wires less conducting than thicker wires. The increase in the piezoelectric coefficient depends on the nanowire radius and length and the increase in surface atoms [60].

The effective piezoelectric constant of a ZnO nanowire does not depend solely on the diameter of the wire, mainly because after a certain limit the increase in the surface-to-volume ratio is compensated for by an increase in wire length [61, 62]. The piezoelectric coefficient of nanowires can be calculated considering it as a one-dimensional structure. With number of atoms 'N' and the super cell volume 'Vscell', the average atomic piezoelectric coefficient can be defined as:

$$e^{a}_{33} = e_{33} \times Vscell/N$$

Table 2 shows the unrelaxed (D_0) and relaxed (D) diameters, the lattice constants (C), strain energy (E), band gap (Eg), Young's modulus (E_3) and effective piezoelectric constant (e^{a}_{33}) of different-sized nanowires as compared to bulk nanowires, as found by Xiang et al. [63].

The significantly higher piezoelectric coefficient of the nanowires is due to large surface-to-volume ratios or larger boundaries as against those of bulk ZnO. The lateral lattice constants remain fixed when strained along the c-axis, and there is no free lateral relaxation of atoms in bulk ZnO. In the case of the nanowire's elongation or compression along the c-axis, free boundaries lead to the lateral relaxation of the atoms. This causes the effective piezoelectric coefficient to increase to:

$$e^{a}_{33} = e^{b}_{33} - e^{b}_{31} \mathbf{x} \upsilon. \quad (1)$$

where υ = Poisson's ratio = $- \epsilon_1/\epsilon_3 = - \epsilon_2/\epsilon_3$, and:

$$\epsilon_1 = \epsilon_2 = (a - a_0)/a_0 \quad (2)$$
$$\epsilon_3 = (c - c_0)/c_0 \quad (3)$$

where 'a' is the relaxed lateral lattice constant, when the lattice constant of ZnO changes to 'c'.

$\upsilon > 0$ results in $e^{b}_{31} < 0$ [64],
and therefore $e^{a}_{33} > e^{b}_{33}$

	A	B	C	D	E	bulk
D_0 (Å)	3.66	9.68	15.96	22.27	28.59	
D (Å)	3.32	9.32	15.61	21.97	28.33	
c (Å)	5.335	5.302	5.27	5.234	5.215	5.180
E_g (eV)	2.40	1.54	1.09	0.85	0.75	0.63
E_3 (GPa)	363	242	217	189	182	147
e^{a}_{33} (10^{-16} CÅ)	2025	1837	1879	1986	1961	1453

Table 2. The unrelaxed (D_0) and relaxed (D) diameters, lattice constants (C), strain energy (E), band gap (Eg), Young's modulus (E_3) and effective piezoelectric constant (e^{a}_{33}) of different sized nanowires as compared to bulk nanowires [62] .

i.e., the piezoelectric coefficient of nanowire is larger than its bulk form.

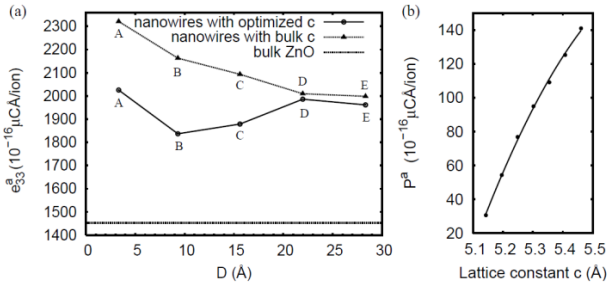

Figure 3. (a) Variation in an effective piezoelectric constant with an increase in wire diameter as compared to its bulk value [63].

Figure 3 shows the relation of the effective piezoelectric constant e^{a}_{33} of ZnO on wire diameter with an optimized lattice constant c against its bulk value. It can be seen that the effective piezoelectric coefficient does not solely depend on the wire radius if the lattice constant is optimized. This implies that the effective piezoelectric constant depends on the wire diameter as well as the relative lattice constant at that diameter. However, for larger diameter nanowires (~20 Å), the piezoelectric coefficients have very similar values both with and without lattice constant optimization. Nonetheless, for a constant bulk value of a lattice constant, the increase in the effective piezoelectric coefficient with decreasing nanowire diameter is linear.

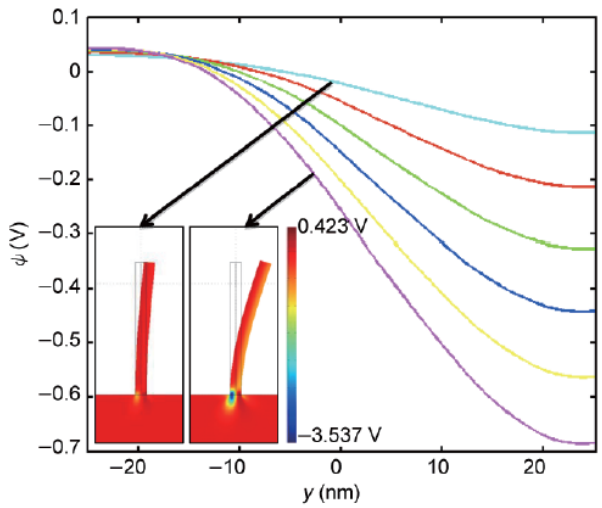

Figure 4. Piezoelectric potential and the colour-plot of the calculated potential at a cross section of x=0 for F=40 nN and F=140 nN [66].

The piezopotential generated across a ZnO nanowire can be significantly affected by factors like the magnitude of the applied bending force, the dimensions and donor concentration. This was theoretically estimated by modelling a ZnO nanowire as a cylindrical structure and by applying a uniform horizontal force on its top surface and then performing the finite element method analysis

of Mantini et al. [65]. The potential generated increases with an increase in the applied bending force. This is because of the increased polarization due to increased strain and the resulting increase in charge accumulation on the nanowire surface. Figure 4 shows the relative change in electric potential generated under increasing bending force for a ZnO nanowire under FEM analysis.

The nanowire diameter significantly affects the piezopotential generated and decreases with an increase in radius. This can be attributed to the fact that the decrease in the radius effectively reduces the applied force. Beyond a certain height, the wire dimension does not affect the electrical potential generated. This is shown in Figure 5, below.

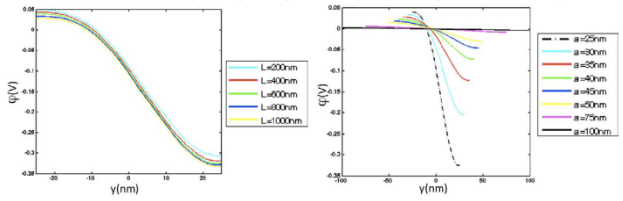

Figure 5. Piezoelectric potential for different lengths of the nanowire and piezoelectric potential for different radii of the nanowire [66].

The donor concentration should be lower than 10^{18} cm^{-3} so as to prevent the complete screening of the piezopotentials generated. When a ZnO nanowire is laterally bent then, along with the positive and negative charge accumulation on its elongated and compressed sides respectively, conduction band electrons also gather near the positive side due to band gap reduction. This causes a partial cancellation between opposite charges. This screening effect is significantly lower on the negative side because of a low donor concentration on n-type nanowires [67]. A n-type 600 nm length ZnO nanowire with a diameter of 50 nm and donor concentration of $1x10^{17}$ cm^{-3} produced a potential less than 0.05 V in the positive side and a negative potential of -0.3 V when a bending force of 80 nN was applied [68].

The mechanical properties of piezoelectric structures are important in a design and reliability context. The elasticity and tensility are important factors in making devices more reliable. ZnO nanowires also display improved resilience compared to their bulk counterparts. They show increased stretching and bending strengths for decreasing diameters between 80-20 nms. Figure 6 shows the SEM images of a ZnO nanowire with a diameter of 20 nms being subjected to a tensile test, and it was found that this particular nanowire could easily sustain a tensile force of up to 3.05 μN. This makes them very favourable for piezopotential generation applications. It ensures that these nanowires can be subjected to high deformation forces and can be repeatedly used for energy harvesting without breaking them.

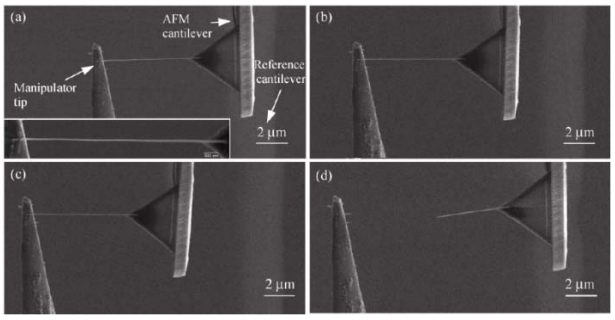

Figure 6. (a–c): Tensile test for ZnO nanowire with a diameter of 20 nm. A high resolution SEM image of the nanowire used for this test is shown in the inset of (d) SEM image showing fractured NW at a tensile force of more than 3.05 μN [68].

Figure 7 shows the same nanowire under a buckling test. The critical buckling force was reported to be 62 nN [69]. For ultrathin diameters (0.7–1.1 nm), ZnO nanowires show an increase in the stress-strain relation, yielding stress and Young's modulus with decreasing size [70].

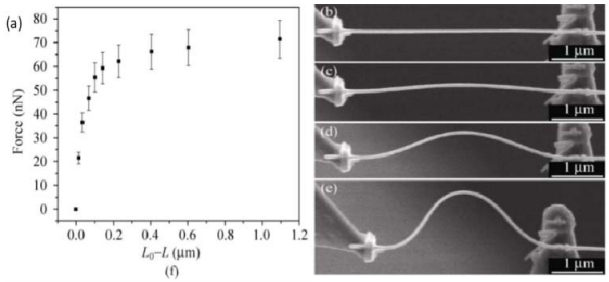

Figure 7. (a) Plot of the variation of the applied force on the nanowire against the axial displacement and (b–e) SEM images of a nanowire under continuously increasing compressive load showing the modulus of the elasticity of the nanowires. A nanowire of a diameter of 20 nm could withstand a force of 62 nN [68].

4. Piezoelectric power-generating devices using ZnO

A single nanowire can act as a diode and when under mechanical strain can pass the charges generated to an external circuit under favourable conditions. It conducts in one direction only, as metal/ZnO contacts mostly result in metal-semiconductor Schottky contacts, giving a unidirectional flow of current in the external circuit [71, 72]. The current and power produced by a single nanowire are not enough for real devices. The integration of a large number of nanowires has been done in an effort to increase the output power. Key issues for harvesting piezoelectric energy included the simultaneous generation of piezoelectric potential in a large number of nanowires, the extraction of that energy and the application of the same to an external load.

4.1 ZnO-based nano-generators using hard substrates

Since the potential developed in a strained nanowire is highest at the side tips and remains there for as long as the wire is under strain, it is important for the top electrode to

touch the wires at their tips while in deformed state. A zigzag silicon electrode with a metal layer can serve this purpose, as shown in Figure 8. Subjecting such an arrangement on a 2 mm² area to ultrasonic vibrations of 41 KHz resulted in an output current of a few nano-amperes [73]. This arrangement showed a steady current when energized by an external voltage source, and this steady current showed a sudden increase in magnitude once it was subjected to ultrasonic waves. The rise in energy was found to be constant for a period of about one hour. The same experiment, when repeated with CNTs, did not give an increase in current, which meant that CNTs - unlike ZnO - did not have piezoelectricity generation capacities.

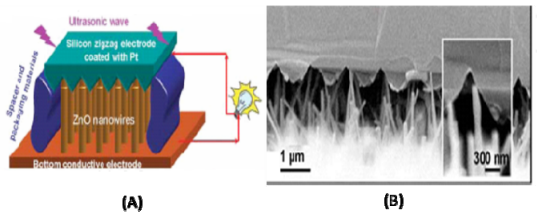

Figure 8. (A) Schematic diagram showing the design and structure of the nano-generator built using ZnO nanowires and a platinum-coated Si zigzag electrode. (B) Cross-sectional SEM image of the nano-generator, made of aligned ZnO nanowires and a platinum-coated Si zigzag electrode [72].

4.2 ZnO-based nano-generators using fibres

ZnO nanowires can act as piezoelectric energy scavengers not only at high frequencies but also at frequencies as low as 10 Hz. This was achieved by growing radial ZnO nanowires of diameters 50~200 nm and about 3.5 μm height on two Kevlar 129 fibres [74], which are lightweight, high-performance and high-tenacity yarns used in motorcycle racing gear, life protection accessories, ropes and cables, and the high-pressure hoses used in the oil and gas industry [75]. A 300 nm thick Au layer coating was applied on the ZnO nanowires on one of the polyamide fibres. The two fibres were then entangled and moved so that the nanowires brushed across each other and piezoelectric energy was generated by the nanowires without a gold coating due to the inherent piezoelectric nature of the ZnO nanowires. The ZnO nanowires with an Au layer coating, however, could not generate piezoelectric energy, as they were very stiff due to the coating and could not be bent by the applied mechanical force. With the metallic gold coating, it acted as an electrode for collecting and transporting charges through an external electrical measurement circuit. The schematic of the arrangement is shown in Figure 9.

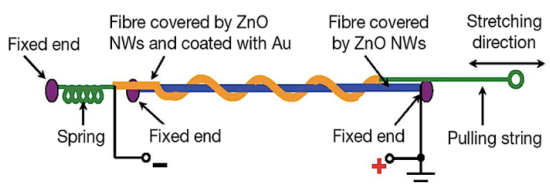

Figure 9. Schematic arrangement for energy generation with radially-grown ZnO nanowires on polyamide fibres [73].

Each time, the negative potential is picked up by the gold coating on the other ZnO wires and a current of about 5 pA is found to be flowing in the external circuit. If the stretching direction is reversed, the direction of current changes and - as a result - bidirectional current can be made to flow in the external circuit by changing the stretching direction. The open circuit voltage measured was found to be about 1~3 mV. It was seen that the short circuit current could be significantly multiplied by increasing the number of fibres used. The current generation mechanism is explained by the schematics in Figure 10.

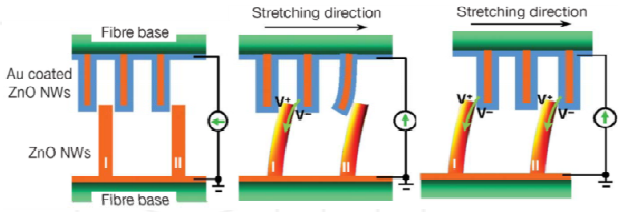

Figure 10. Schematics showing the generation and tapping of piezoelectric current by entangling flexible fibres with radially-grown ZnO nanowires [73].

4.3 ZnO-based nano-generators using flexible substrates

The substrates on which ZnO nanowires are grown are usually hard and brittle. The use of flexible substrates with piezoelectric ZnO nanowires would mean that the nanowires could be deformed by bending the substrate. If the flexible substrates are made conductive, then they could be used in systems requiring foldable power sources, like foldable electronics or even wearable or implantable biomedical devices for the human body. If the substrate used is a plastic, they could be lightweight, flexible and economical, and if a polymer were to be used then they would be biocompatible as well as biodegradable. Moreover, it would be capable of harvesting energy from environmental vibrations or human body movements like breathing, blood flow, physical actions and movement, etc. [76].

The first successful piezoelectric nano-generator on a flexible substrate used vertical nanowires and was reported by Gao et al [75]. ZnO nanowires were synthesized on a conductive plastic substrate. The density and distribution was controlled using a catalyst according to a predetermined design. The adhesion of the nanowires on the substrate was improved by spinning a thin layer of polymer on the substrate after wire growth, and their roots were partially embedded. Electrical energy generated from this setup using an AFM tip was found to be ~20 mV at a power density of 1-2 pWμm⁻², 0.1-0.2 mWcm⁻². A maximum of 5 pW power could be attained at an output voltage of 45 mV with this nano-generation setup. Figure 11 shows the detailed images of the vertical ZnO nanowires grown on flexible substrates.

Though the piezoelectric nano-generator described above had a flexible substrate, substrate bending was not used for energy generation purposes. Instead, an AFM tip was used to bend the nanowires. Choi et al. [77] reported fabrication of mechanically-powered, fully-integrated, transparent, flexible, charge-generating nanodevices with piezoelectric nanorods that could be used as pressure sensors. ZnO nanorods were grown on flexible ITO-coated polyethersulfone or a PES substrate and the top electrodes were made of palladium gold while indium tin oxide-coated flexible substrates were used, thus making it fully flexible. Figure 12 shows the schematic of the device with a SEM image of the ZnO nanorods, the final sealed device and its transparency. With a size of 3 cm^2, the device generated a current density of ~1 $\mu A/cm^2$ when subjected to a mechanical pressure of 0.9 Kgf and so acted as a pressure sensor.

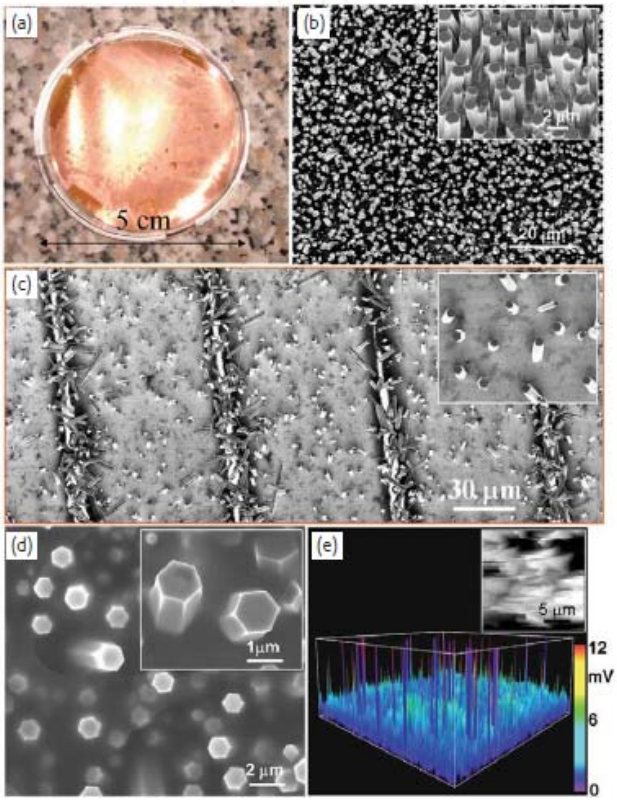

Figure 11. (a) Optical image of aligned ZnO NWs grown on a polymer substrate. (b) SEM image of ZnO NWs synthesized using a chemical approach. (c) SEM image of ZnO NWs grown on a patterned substrate. (d) Top view SEM image showing aligned ZnO wires on a plastic substrate coated with poly(methyl methacrylate) - or PMMA - for reinforcement. Inset: enlarged view of the PMMA encapsulated microwires. (e) Corresponding voltage output profile under AFM measurement. Inset: topography image of the 20 μm x 20 μm area [75].

In the case of a foldable piezo-energy harvester, maximum deformation will be imparted on to the ZnO nanowires by placing the nanowires on the bendable substrate laterally and not vertically. A single nanowire power generator can be made flexible to acquire improved stability, mechanical robustness, lifetime and environmental impact. This can be done by packaging a nanowire on a flexible substrate and attaching it firmly to metal electrodes at both ends. The piezopotential can be generated by bending and releasing the thin flexible substrate of insulating wax. This mechanical strain induced results in the electron flow in an external circuit. The current remains for so long as the wire remains deformed.

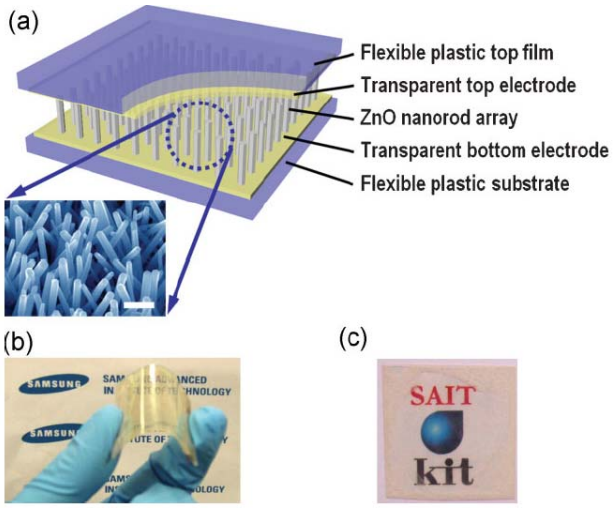

Figure 12. (a) A fully integrated transparent piezoelectric device (SEM image of ZnO nanowires inset), (b) flexibility test and (c) transparency test [76].

Yang et al. [78] reported a flexible nanogenerator prepared by laterally bonding a piezoelectric fine wire of ZnO onto a kapton polyimide film with the help of silver paste. Schottky contacts were created at the two edges of the wire, thereby preventing the electrons from flowing through the nanowire and facilitating conduction in the external circuit when stretched. Output voltage values as high as 50 mV could be achieved from a single nanowire. Since the nanowires had much thinner diameters (~4 microns) as compared to the substrate thickness (~200 microns), the bending of the substrate led to tensile stress across the axis of the NW. As ZnO is a piezoelectric material, a piezoelectric field is created along the length of the stressed NW, generating a positive potential on the stretched side. This results in a flow of charge carriers in the external circuit, while the Schottky contacts at the ends stopped the carriers from flowing in the opposite direction or else through the NW. On the other hand, the releasing of the substrate resulted in an opposite polarity along the NW, giving rise to alternating voltage generation in the output circuit. Figure 13 gives the schematic arrangements for the single wire nano-generator on a flexible substrate, mechanical bending, measurement setup and packaging setup.

These piezoelectric fine wire nano-generators on a flexible substrate have sizes much larger than a regular ZnO

nanowire. A PFW with a diameter of approximately 4 microns and a height of 200 microns could generate an output voltage of 20~50 mV.

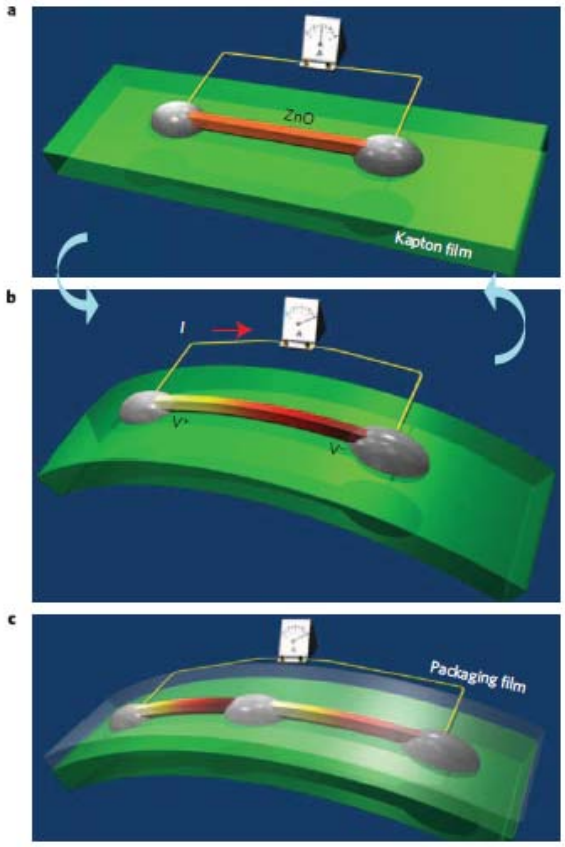

Figure 13. Design of a piezoelectric fine wire (PFW) generator on a flexible substrate. (a) The PFW lies on a polymer (Kapton) substrate, with both ends tightly-bonded to the substrate and outlet interconnects. (b) The mechanical bending of the substrate creates a tensile strain and a corresponding piezoelectric potential in the PFW, driving electrons through the external load. (c) The wires are connected in series and packaged in a flexible polymer film [77].

By making an array of such lateral ZnO nanowires, higher output voltages capable of driving small commercial electronic devices were produced by Zhu et al. [79]. An open circuit voltage of 2.03 V and a peak output power density of 11 mW/cm^2 was produced by forming horizontally-aligned arrays and depositing parallel electrodes to connect them. The energy generated was stored using capacitors and then to light up commercial LEDs. It was predicted that with further optimization of the NW density on the substrate and the integration of many layers of these arrays, it would be possible to give outputs of 0.44 mW/cm^2 and a volume density of 1.1 mW/cm^3. Figure 14 shows a schematic depicting the working principle of this nano-generator.

Lee et al. [80] demonstrated a fully stand-alone, self-powered device that could sense the presence of Hg^{2+} ions in a water solution powered by a ZnO nanowire array on a flexible kapton substrate. Another kapton film, coated with a thin layer of gold, was used as the electrode. The mechanical bending of this nano-generator resulted in an output voltage of about 350 mV and a current density of about 125 nA cm^{-2}. This was used for sensing mercury ions in water with the addition of a rectifier circuit and a capacitor for charge storage.

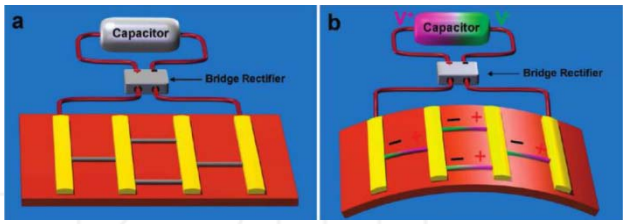

Figure 14. Working principle and output measurement of the HONG. (a) Schematic diagram of HONG's structure without mechanical deformation, in which gold is used to form Schottky contacts with the ZnO NW arrays. (b) Demonstration of the output scaling-up when mechanical deformation is induced, where the '+/-' symbols indicate the polarity of the local piezoelectric potential created in the NWs [78].

Although plastic substrates are very useful for flexible piezotronics and promise to be the major substrate materials for self-powered systems, it has been found that recently-used materials, like polyethylene terephthalate (PET), polyethersulfone (PES) and polyethylene naphthalate (PEN), do not have high thermal stability. This is mainly due to the differences in the coefficients of thermal expansion between the polymer substrates and the inorganic layers on them. As a result, thermal stresses are induced among the different layers as the temperature increases, which eventually leads to unstable electrical outputs. Hence, for the better thermal stability of these systems, cellulose-based substrates can be used. This substrate is easily available, light and can provide much-needed flexibility [81].

4.4 High efficiency nano-generators

In order to increase the voltage and power outputs, a large number of nanowire energy harvesters were integrated and aligned and their charging/discharging processes synchronized. The vertical and lateral alignment of nanowires in the structured array could be used to generate sufficient power to drive real devices. 700 rows of nanowires were integrated by Xu et al. [82] to produce a peak voltage of 1.26 V - sufficient to drive an AA battery. The vertical integration of three layers of nanowires produced an output voltage of up to 0.243 V and an output power density of 2.7 mW/cm^3. The peculiarity of this high output device was that the nanowire ends were solidly bonded to the electrodes. The vertically-integrated system was used to power a pH sensor and an UV sensor. The vertical integration scheme and the output voltages are shown in Figure 15.

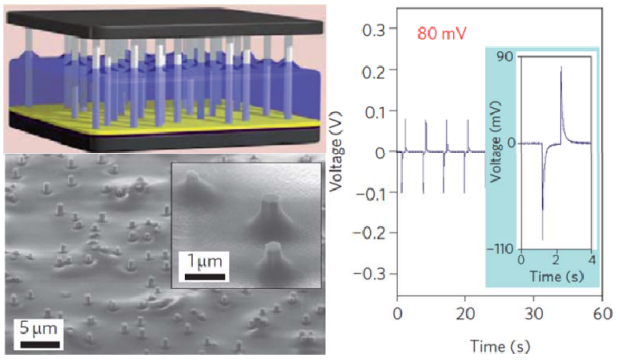

Figure 15. Integrated nano-generator schematic with vertically-aligned ZnO nanowires on a gold-coated flat surface. Both electrodes are separated by a PMMA layer. A platinum-coated flat electrode is placed on top of the nanowires. The SEM image of the nanowire array immersed in PMMA with its tips exposed greatly improved the robustness of the structure and the corresponding voltage of the system generated due to exposure to mechanical forces [81].

The lateral integration of nanowires was performed to add AC voltages constructively for high output. Aligned nanowires were fabricated parallel to the surface and 700 such nanowires were integrated with a Schottky contact on one side. This led to an output voltage of 1.26 V, with a maximum current of 28.8 nA. If highly-aligned nanowires are subjected to external forces simultaneously, each nanowire will develop a potential gradient across its c-axis. Because the c-axes of the nanowires were well aligned in parallel, the generated piezopotentials were distributed in a similar manner and along the same direction, as they were subjected to a uniform strain uniaxially. This led to enhanced macroscopic *piezopotential* generation. Figure 16 shows the schematic, voltage generated, current generated and SEM micrograph of the lateral integration of nanowires for improved piezoelectric output.

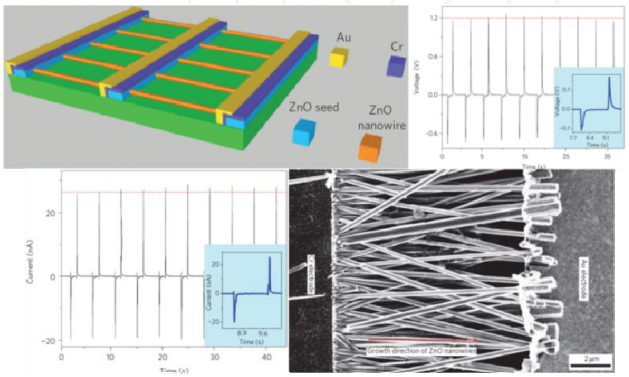

Figure 16. Integration of laterally-aligned nanowires. Schematic, voltage generated, current generated and SEM micrograph (clockwise) [81].

5. Nano-generators using other materials

While ZnO nanowires had been the principal material for the exploitation of piezoelectric energy generation, some other ceramic crystals and polymer materials have been used for the same purpose at the bulk level and have been demonstrated to give good power generation at the atomic-scale as well. Nano-generators built using nanofibres of PZT and PVDF have been reported and have attracted attention in research [83]. In this section, we discuss the various efforts for energy harvesting using such materials for different devices and self-powered systems.

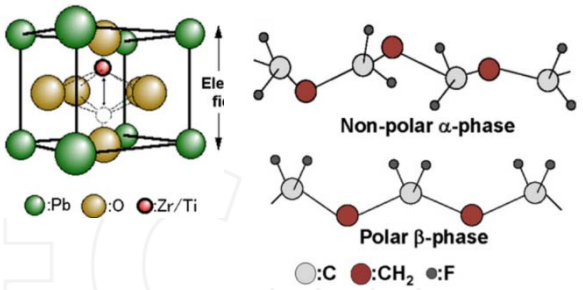

Figure 17. (Left) Schematic of the polar crystal structure of PZT and (Right) the schematics of the non-polar and polar structures of PVDF [84].

The most common ceramic material used for piezoelectric energy harvesting is lead zirconium titanate (or PZT) [85]. It has exceptional piezoelectric properties. However, to enhance the piezoelectric properties of PZT, it must be annealed at high temperatures of more than 600°C [86]. In addition, the energy conversion efficiency of PZT nanofibres is low because of a complex manufacturing process that leaves them diluted [87]. Another material used for nano-scale energy harvesting is a polymer, polyvinylidene fluoride (or PVDF) [88]. Organic nanofibres of PVDF are lightweight, flexible, bio-compatible and can be produced in different sizes and shapes [89]. PZT comes with an inherent polar crystalline structure, like ZnO, while PVDF needs to be converted from a non-polar α-phase to a polar β-phase by applying an electric field through a process called 'poling'. The resilience of PZT increases with a decrease in size, countering the problem of fragility associated with it as compared to PVDF. Figure 17 shows the atomic arrangements of these materials schematically.

5.1 Nano-generators using PZT

Lead zirconate titanate (PZT) has been used for piezoelectric energy generation at the macro-scale. PZT nanofibres are found to have a higher piezoelectric voltage constant than semiconducting nanowires due to their inherent polar crystal structure and high dielectric value, and they can be synthesized with a very high aspect ratio. However, bulk PZT and its thin films are extremely fragile, and are not useful for energy generation under alternating loads. They have been found to be very sensitive to high frequency. The problem of fragility, however, disappears for high aspect ratio nanostructures [90, 91].

Chen et al. [92] demonstrated the possibility of harvesting piezoelectric energy using PZT nanomaterials. PZT nanofibres with a length and diameter of 500 μm and 60 nm respectively were laterally aligned on platinum, fine wire interdigitated electrodes, and packaged using a soft polymer of polydimethylsiloxane (or PDMS) on a silicon substrate. Under the application of periodic stress, this nano-generator produced a voltage of 1.63 V and a power of 0.03 μW at a load resistance of 6 MΩ Figure 18 shows the schematic arrangement of the PZT nanofibre-based nano-generator, the piezoelectric voltage generation process and measured voltage generated as a result of applied force.

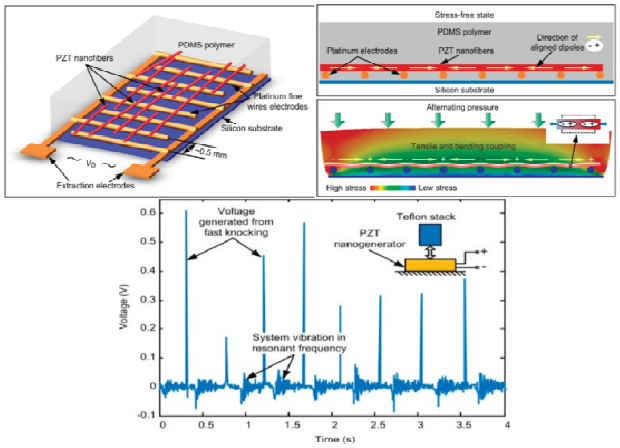

Figure 18. Schematic arrangement of a PZT nanofibre-based nano-generator, the distribution of forces for piezoelectric voltage generation and voltage generated as a result of applied force (clockwise) [91].

Xu et al. [2] have demonstrated how epitaxially-grown PZT nanowire arrays could be used for high output piezo-energy harvesting and the possibility of using such energy harvesters for mobile electronic devices. A single array of such nanowires grown at 230°C produced a peak output voltage of ~0.7 V and a current density of 4 μAcm^{-2}, with an average power density of 2.8 mWcm^{-3}. The alternating current generated was rectified and stored, and used for lighting a commercial laser diode.

Wu et al. [93] have reported on a textile nano-generator built using PZT nanowires that could be used for wearable and self-powered devices. A generator thus built could generate an output voltage of 6 V and produce a current of 45 nA. The nano-generator was built cost effectively and was demonstrated to light a commercial LCD and power a ZnO nanowire UV sensor for the quantitative detection of UV light.

5.2 Nano-generators using PVDF

For the first time, polyvinylidene fluoride (or PVDF) nanofibres were directly written using a near-field electrospinning process by Chang et al. [94] Piezoelectric properties were produced and tested by electrical poling and *in situ* mechanical stretching. Repeatable and consistent electrical output voltages up to 8.5 mV with an output power of 7.2 pW were achieved under the mechanical stretching of a single electrospun PVDF nanofibre. The energy conversion efficiency was found to be much higher than PVDF thin films [94, 95].

Hansen et al. [96] demonstrated a hybrid nano-generator made of a piezoelectric nanofibre of polyvinylidene fluoride (PVDF) for mechanical energy harvesting and a flexible bio fuel cell for harvesting biochemical energy in biofluid, with both devices capable of working either independently or simultaneously. This hybrid nano-generator was used to drive a single nanowire-based UV sensor to build a self-powered system. Figure 19 schematically illustrates the working principle of this device and the measured voltages for the same.

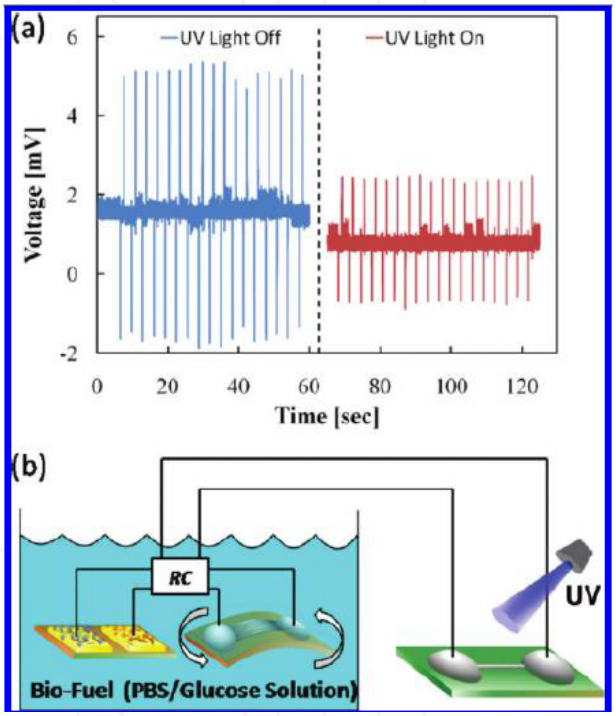

Figure 19. Integration of the hybrid BFC-NG device with a UV nanosensor to demonstrate a "self-powered" nanosystem. (a) The voltage drop across the ZnO NW UV light sensor when the UV light is off and on. For illustration purposes, only stabilized signals are displayed. (b) Schematic illustration of the self-powered hybrid nanosystem [95].

5.3 Nano-generators using barium titanate

The most recent material to be reported for piezoelectric power generation is perovskite $BaTiO_3$, which is not only piezoelectric but also ferroelectric. Park et al. [97] have demonstrated the use of $BaTiO_3$ thin films on a flexible substrate for the conversion of mechanical energy into electrical energy for the first time. They used radio frequency magnetron sputtering to deposit $BaTiO_3$ thin

films under an electric field of 100 kV/cm on a Pt/Ti/SiO_2 substrate. The ribbon-structured thin films were transferred onto a flexible substrate using standard microfabrication and lithographic printing techniques, and connected by interdigitated electrodes. By applying a periodic bending force, the nano-generator produced an output current density of 0.19 μA/cm^2 and a power density of ~7 mW/cm^3. Figure 20 gives the schematic of the fabrication procedure of the nano-generator.

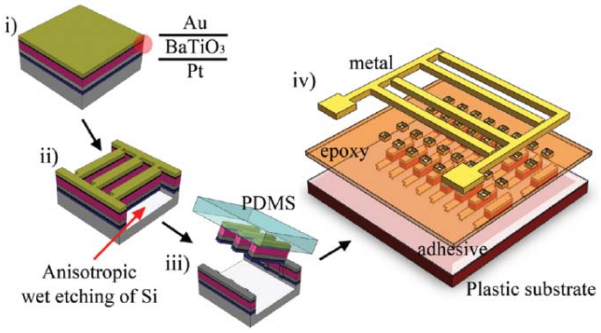

Figure 20. Schematic illustration of the process for fabricating a flexible $BaTiO_3$ nano-generator on plastic substrates [96].

The analysis of piezoelectric potential distribution was done for the thin film. The results obtained are shown in Figure 21. It was found that when stretched from both ends, the potential increased from the bottom of the thin field (at 0 V), which is connected to the substrate, to a maximum of 0.529 V at the topmost layer.

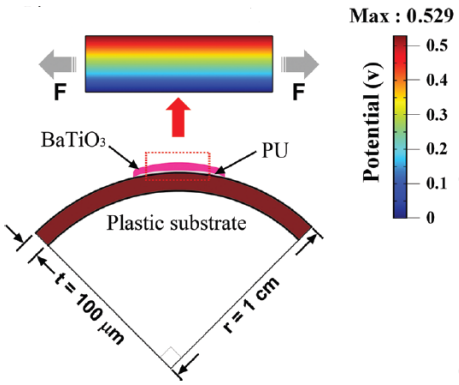

Figure 21. The calculated piezoelectric potential distribution inside the BaTiO3 thin film. A pure tensile strain is assumed to exist in the thin film when the substrate is bent over 90° with a radius of 1.0 cm. The piezoelectric potential difference inside the $BaTiO_3$ thin film is 0.529 V [96].

6. Summary and conclusion

Conventional power sources and batteries cannot be integrated with micro-/nanosystems and need periodic replacement or recharging. In addition, they can be very bulky in size and weight as compared to the parent device. Accordingly, we looked into piezoelectric energy harvesters, which promise to be a solution to such power problems.

Wireless devices may allow *in situ*, real-time biomedical monitoring, but such devices still require a power source. Ideally, such devices should be self-powered rather than using a battery. The human body provides numerous potential energy sources – mechanical energy, like body movements, muscle stretching and blood pressure, etc., and hydraulic energy, like blood flow and blood vessel contraction, etc. Nature is also abundant with vibrational energy in the form of acoustics, ultrasonics and hydraulic energy, like dynamic fluids, etc.

In this work, we looked into the details of the technology of piezoelectric nanostructures used for the generation of piezopotential in order to convert it into electrical energy for use in developing self-powered nanosystems. The efficient conversion of this energy into electric energy at the macro-scale is a challenge. Objective research in this direction is gradually leading us towards such power sources, and we look to a future of integrated nanosystems of greatly-reduced size for optoelectronics, biosensors, resonators and medical electronics, etc. Self-powered devices for the *in situ* implantation for bio-sensing, biomedical monitoring, diagnostics and therapy, are also being investigated and successfully demonstrated.

Piezoelectricity is naturally available in certain ceramics and crystals. Certain polymers have also been used for piezo-energy harvesting. We had explored the various materials in use to date for energy harvesting at the micro- and nano-scales. Although ZnO is the most widely used crystal material for this purpose, some ceramics and polymers have also been used for the same purpose. PZT is the most widely used ceramic material, while a polymer material PVDF has been used too. $BaTiO_3$ is the most recent material being used for piezo-energy harvesting. The relative merits and de-merits of different materials as seen through different research works are discussed below.

Ceramic materials like PZT and $BaTiO_3$ have high piezoelectric sensitivity and coupling coefficients. They are available commercially at low cost and in a variety of designs. However, stability is an issue for them, as they suffer from the loss of polarization with continued usage. The piezoelectric properties are also strongly dependent on the operating temperatures. Electrical charge separation can occur not just from mechanical deformation but with temperature changes as well. These are brittle substances; hence, they cannot withstand mechanical deformation for long. Piezoelectric single crystal materials (ZnO) are easily synthesized in the required sizes and shapes, and very economically too. They have a high piezoelectric coefficient and electromechanical coupling. ZnO is highly tensile and can thus undergo huge mechanical deformations for a long

period of time. The piezoelectric properties are not temperature-dependent and so can be operated in higher temperature environments.

Polymers, on the other hand, are not inherently polarized and undergo polarization with the application of an external field in a special environment. However, because of their properties of being light-weight, flexible and biocompatible, they are increasingly seen as potential wearable and foldable energy harvesters for various biomedical applications and are attracting research.

ZnO nanowires had been the most widely used material for nano-energy harvesting. We found that, throughout the reported research work done up until now and referenced above for nano-energy harvesting, ZnO holds the following advantages over other materials:

- ZnO is a versatile metal oxide semiconductor material with inherent piezoelectricity and semiconducting properties.
- The piezoelectric properties improve for nanostructures as compared to bulk ZnO.
- Synthesizing one-dimensional ZnO nanostructures can be done economically at room temperature.
- These nanostructures can not only withstand huge deformations, but so too can their mechanical properties - like resilience and tensility - improve with size reduction.
- They can be synthesized on any substrate and can generate piezopotentials under any type of vibration.

It has been found that placing ZnO nanorods on hard substrates limits their usage to devices that can be subjected to vibration externally. Foldable, wearable, self-powered systems are possible if these nano-generators are built on flexible substrates. The following advantages are easily achievable by growing ZnO nanowires on plastic substrates:

1. Large deformations are possible not only on the nanowires but also on the substrates.
2. They can be used as foldable power sources for self-powered systems.
3. Because of the huge deformations applicable, a large output power could be expected.
4. It can be implanted into the human body, for the self-powering of implanted medical devices.
5. Human body movements can be used for energy generation.

These facts have led research groups to carry out extensive studies on using conducting flexible substrates for piezoelectric energy harvesters. Energy harvesters using nanostructures synthesized on flexible substrates - like PET, PEN and PES - were demonstrated. Piezoelectric wires were also placed laterally on flexible substrates and made to bend along with the substrate, giving significant output voltages. The output power generated by piezoelectric nano-generators were not enough to drive practical circuits. Efforts were made in creating arrays of nanowires to get better output power. These were designed for increased voltage outputs as well as for current increase. Soldered and/or interdigitated electrodes for picking up piezo-generated signals and fixing them to laterally-placed nanowires resulted in highly-enhanced power outputs.

Table 3 below briefly summarizes the various nano-generating devices reported up to now. It draws a comparison between their performances with respect to the materials used and various devices' operational parameters.

It can be seen from the table that open circuit voltages from a few millivolts to a few volts have been achieved with all types of materials. The increased output voltage mostly depends on two factors: (1) on the simultaneous generation of charges, which again depends on the nanostructure alignment and uniform application of deformation force, and (2) on the efficient extraction of the generated charges, which depends on the electrodes touching the tip of the nanowires at the time of charge separation, preferably on one side only so as to prevent the cancellation of opposite charges, and before the strain is removed from the piezo-generating structures. These conditions are met when the electrodes are soldered onto the nanostructures and - as can be seen from the table - the output voltage is on the higher side for soldered electrodes. The output current densities have also been improved over the years, using arrays of nanostructures in parallel and connecting them through interdigitated electrodes. The current densities have gone up from a few pico-amperes to a few micro-amperes per square centimetre area. This enhancement of output power has resulted in stand-alone self-powered systems being demonstrated by research groups. A self-powered mercury ion sensor and pressure sensor have recently been demonstrated.

The current generation by piezotronic devices reported to date is very low, being mostly within the pico- to nano-ampere range. Hence, the total power generated by arrays of piezoelectric nanorods is not sufficient for more than a few targeted applications, like sensors. However, LEDs and LCDs have been demonstrated to light up with the proper storage of energy harvested from piezoelectric nano-harvesters.

7. References

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