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Flexible Piezoelectric Thin-Film Energy Harvesters and Nanosensors for Biomedical Applications

*Geon-Tae Hwang, Myunghwan Byun, Chang Kyu Jeong, and Keon Jae Lee**

The use of inorganic-based flexible piezoelectric thin films for biomedical applications has been actively reported due to their advantages of highly piezoelectric, pliable, slim, lightweight, and biocompatible properties. The piezoelectric thin films on plastic substrates can convert ambient mechanical energy into electric signals, even responding to tiny movements on corrugated surfaces of internal organs and nanoscale biomechanical vibrations caused by acoustic waves. These inherent properties of flexible piezoelectric thin films enable to develop not only self-powered energy harvesters for eliminating batteries of bio-implantable medical devices but also sensitive nanosensors for in vivo diagnosis/therapy systems. This paper provides recent progresses of flexible piezoelectric thin-film harvesters and nanosensors for use in biomedical fields. First, developments of flexible piezoelectric energy-harvesting devices by using high-quality perovskite thin film and innovative flexible fabrication processes are addressed. Second, their biomedical applications are investigated, including self-powered cardiac pacemaker, acoustic nanosensor for biomimetic artificial hair cells, in vivo energy harvester driven by organ movements, and mechanical sensor for detecting nanoscale cellular deflections. At the end, future perspective of a self-powered flexible biomedical system is also briefly discussed with relation to the latest advancements of flexible electronics.

1. Introduction

Implantable biomedical electronics have recently gained huge interest in light of increasing the quality of life and extending the lifespan of patients. The implantable devices are currently used in a wide variety of parts in the human body as artificial remedy tools, with applications including cardiac pacemakers,[1] implantable cardioverter defibrillators (ICDs),[2] deep brain stimulation (DBS),[3] and artificial retinas[4] as illustrated in **Figure 1**. The bioelectronics can provide real-time treatment (e.g., stimulation of muscle and nerve) and diagnosis (e.g., heart rate monitoring) for various diseases related with the heart, brain, and sensory organs: for example, a cardiac pacemaker can regulate the heartbeat by using electrical stimulation to contract the cardiac muscle of patients who suffer from heart blockage or sick sinus syndrome, which causes an abnormal heart rate.[5] Although advancements in current battery technology for biomedical devices have led to significant enhancement in storage capacity and size reduction, the operational lifespan of batteries is still limited to several years (e.g., 7 to 10 years for a cardiac pacemaker and 3 to 5 years for DBS) and additional surgeries for periodic replacement of the batteries are inevitable.[6,7] Such surgeries, however, can potentially give rise to health risks, such as infection and bleeding during the procedures, and financial burdens for the elderly in particular.[8] More efforts and studies to enhance the lifetime of batteries, or even eliminate the batteries from implants, therefore should be made to diminish the medical burden of replacement as well as cost for patients.[9]

Attractive approaches based on self-powered bioimplantable systems have been recently studied to integrate energy-harvesting devices inside the human body for the conversion of biomechanical movements (including cardiac/lung motions, muscle contraction/relaxation, and blood circulation) into electric power.[10–12] In the conversion process of mechanical energy harvesting, various techniques can be used such as electromagnetic induction,[13] a magnetostrictive effect,[14] and a piezoelectric effect at a specific frequency range.[15] However, bulky types of energy-harvesting systems have limited utility as implantable energy sources inside the human body due to incongruent contact with the corrugated and curved surfaces of organs such as the eye, brain, lung, and heart. In addition, energy devices on thick and rigid substrates are unsuitable for responding to the minute movements of internal organs and muscles to scavenge electric energy. Extremely slim, lightweight, and pliable energy harvesters on plastic films such as polyimide (PI), polyethylene terephthalate (PET), and polyethylene naphthalate (PEN), which are widely used as substrates in flexible electronics due to their suitable strength, ductility, and flexibility, are thus required for conformal settlement and energy harvesting on organ

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and muscle surfaces.[16–18] Recent advances in the development of flexible harvesting devices based on piezoelectric materials are an important step for resolving the aforementioned issues.[19,20] In particular, several research teams have fabricated high-performance flexible piezoelectric energy harvesters [called nanogenerators (NGs)] using inorganic thin films such as $BaTiO_3$,[21] $Pb(Zr_x,Ti_{1-x})O_3$ (PZT),[9,22–24] and $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3 - xPbTiO_3$ (PMN-PT).[25] These functional ceramic materials were flexible enough for harvesting electric energy by tiny irregular vibration and mechanical deformation, and are thus potentially applicable to various bioimplantable medical devices.[26] Flexible piezoelectric thin films have also been studied for utilization as robust stimulation tools for muscles/nerves and energy harvesters operated from organ motions.[9,25]

The use of flexible piezoelectric thin films are not only limited to energy harvesters but also include mechanical nanosensors for biomedical applications. These freestanding piezoelectric thin films are very sensitive, to the point of even detecting mechanical nanoscale movements (e.g., vibration caused by acoustic resonance and deformation of biological cells). Recent studies demonstrated sensing of vibrational displacement of 15 nm from audible sound frequency for bio-inspired artificial hair cells and monitoring of volume change of PC12 cells for electromechanical biosensing using flexible piezoelectric thin films that show biocompatible, immediate, and sensitive properties.[26,27] These approaches could be extended to future ubiquitous in vivo biomedical sensing for recovery of the damaged sensorium and real-time monitoring of heartbeat/blood pressure.

This manuscript provides a brief overview of recent progress made in the area of flexible piezoelectric thin-film energy harvesters and nanosensors in the biomedical field. In particular, this review paper focused on introduction of inorganic-based flexible piezoelectric thin films for energy harvesting and sensing applications due to their outstanding piezoelectric properties compared to organic-bases materials. Moreover, the applications of flexible piezoelectric thin films, such as self-powered energy sources, nerves/muscles stimulator, acoustic detector for artificial hair cells, and nanoscale sensor for monitoring cellular volume changes, are discussed.

2. Flexible Piezoelectric Thin-Film Energy Harvesters

In 2006, piezoelectric NGs with ZnO nanowires were proposed by Wang and co-workers as active materials to convert randomly oriented mechanical energy into electric energy.[19] The initial flexible NG based on ZnO nanowire array yielded electrical outputs of 2 V and ≈100 nA by periodic deformation of the device.[28] The mechanism of the flexible NG originates from the piezopotential distributed inside the piezoelectric materials by an external stress, resulting in a momentary flow of electric charges in the external load due to the driving force of the piezoelectric potential.[29,30] The benefit of applying flexible piezoelectric materials is that they can generate electric power by physical movements, and the triggering frequency can be sub-one Hz to thousands of Hz, which is ideal for harvesting random motions in various environmental conditions.[20] The generated power of a NG is strong enough to turn on conventional light-emitting diodes (LEDs) and liquid crystal displays (LCDs).[31–34]

Since 2010, there have been reports on several innovative approaches to transfer crystallized perovskite thin films

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Prof. Keon Jae Lee received his Ph.D. in Materials Science and Engineering (MSE) at University of Illinois, Urbana-Champaign (UIUC). During his Ph.D. at UIUC, he involved in the first co-invention of "Flexible Single-crystalline Inorganic Electronics," using top-down semiconductors and soft lithographic transfer. Since 2009, he has been a professor in MSE at KAIST. His current research topics are self-powered flexible electronic systems including energy harvesting/storage devices, LEDs, large-scale integration (LSI), high-density memory and laser material interaction for in vivo biomedical and flexible applications.

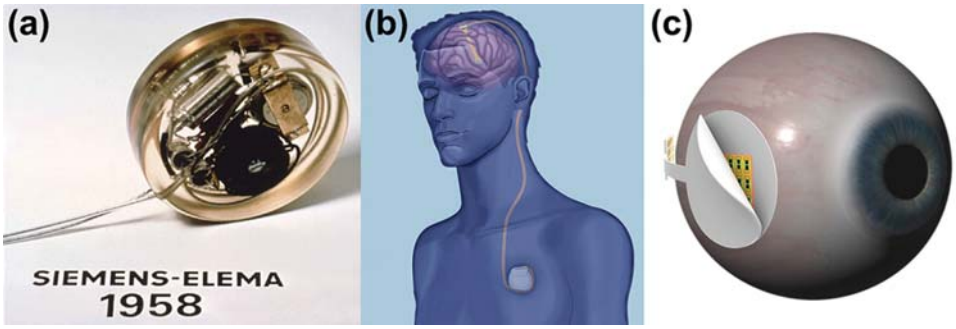

Figure 1. a) The first implantable artificial cardiac pacemaker in 1958. Copyright Siemens. b) Fully implanted deep brain stimulation device. Copyright Ohio State's Wexner Medical Center. c) Artistic illustration of a retinal implant device. Reproduced with permission.[16] Copyright 2013, American Chemical Society.

including $BaTiO_3$, PZT, and PMN-PT onto thin plastic substrates from bulk substrates to exploit high intrinsic piezoelectric properties of inorganic ferroelectric materials as flexible energy harvesters.[21,23–25] To increase the performance of flexible harvesting devices, it is highly desirable to utilize such flexible piezoelectric materials with a high piezoelectric coupling constant (d_{33}), which represents the direct relationship with generated energy density ($w = T^2 \cdot {d_{33}}^2/2\varepsilon$, where w is energy density, T is stress of material, and ε is permittivity at constant stress).[35,36] Generally, most perovskite-structured materials have larger d_{33} values than ZnO nanowires: for example, bulk $BaTiO_3$, PZT, and PMN-PT show three times, 25 times, and 90 times higher d_{33} values than ZnO nanostructures, respectively.[35,37] For this reason, the perovskite piezoelectric thin films have contributed to the realization of high-performance flexible energy-harvesting devices. Furthermore, these flexible piezoelectric thin films allow the development of thin, pliable, and lightweight energy devices on thin single plastic substrates that enable the conversion of tiny movements by filling narrow gaps such as under human skin, at interfaces of organs, and inside rubber tires for harvesting electricity.[38] This section presents emerging developments of flexible piezoelectric thin-film energy harvesters.

2.1. Flexible $BaTiO_3$ Thin-Film Energy Harvester

ABO_3-type perovskite $BaTiO_3$ thin films have garnered attention due to their excellent ferroelectric properties and lead-free eco-compatible characteristics.[39] **Figure 2**a schematically illustrates the fabrication steps of a flexible $BaTiO_3$ thin-film energy harvester on a plastic substrate. This work was innovative because it used high temperature-annealed piezoelectric perovskite thin films for flexible energy harvesters, and in contradistinction to previous nanowire-based NG approaches. A $BaTiO_3$ thin-film deposited on a Pt/Si wafer was annealed at high temperature (700 °C) for crystallization of the amorphous piezoelectric film. After deposition of a top metal electrode, a metal-insulator-metal (MIM) piezoelectric layer was etched by a dry-etching process using narrow bridge patterns, and then the underlying Si layer was removed by anisotropic wet etching to separate MIM ribbons from the bulk substrate. A polydimethylsiloxane stamp was uniformly placed on the top surface of a freestanding MIM array to ink the MIM structures onto the elastomer. Lastly, the MIM ribbons were transferred onto an adhesive-coated plastic substrate and then poled by an electric field of 200 kV cm^{-1}. Figure 2b shows the completed $BaTiO_3$ thin-film NG on thin flexible substrate. The inset displays that the electrodes of the MIM array are connected by metal lines to measure output signals. Figure 2c shows the generated voltage and current of the $BaTiO_3$ thin-film harvester during periodic bending and releasing. Under continual bending/unbending motions of a linear motor, the $BaTiO_3$-harvesting device (total active area of 82 mm^2) generated an open-circuit voltage signal of 0.35 V and a short-circuit current signal of 12 nA. When the $BaTiO_3$ NG was bent by fingers, the device generated current density of 0.19 μA cm^{-2} and power density of 7 mW cm^{-3}. Although this work demonstrated a lead-free perovskite flexible piezoelectric energy harvester with high power density, it accompanies the drawback of a complicated process along with ≈nA level output current due to small active size (individual narrow bridge pattern of 300 μm × 50 μm), caused by wet etching of the sacrificial layer.

2.2. Flexible PZT Thin-Film Energy Harvester

Park et al. reported highly efficient, large-area, flexible PZT thin-film harvesting devices on flexible substrates that were realized using an inorganic-based laser lift-off (ILLO) process.[23,40] PZT is a traditionally preferred piezoelectric material due to its higher electromechanical coupling coefficients than other conventional piezoelectric materials including $BaTiO_3$.[41] The ILLO process eliminates the size limitation of the piezoelectric thin film to increase the electric output power of a flexible energy harvester. In addition, this dry-type transfer technique using an excimer laser is advantageous for production and commercialization of flexible piezoelectric harvesters compared to wet-etching processes, because it can be applied up to Gen 10 glass size (9 feet × 10 feet) with a roll-to-roll process by simple backside irradiation of a laser, technology that has already been commercialized in the display industry such as in the case of low-temperature poly-silicon (LTPS).[42–44] **Figure 3**a schematically illustrates the fabrication process of a flexible PZT thin-film energy harvester using the ILLO process. A highly piezoelectric PZT thin film was formed on a

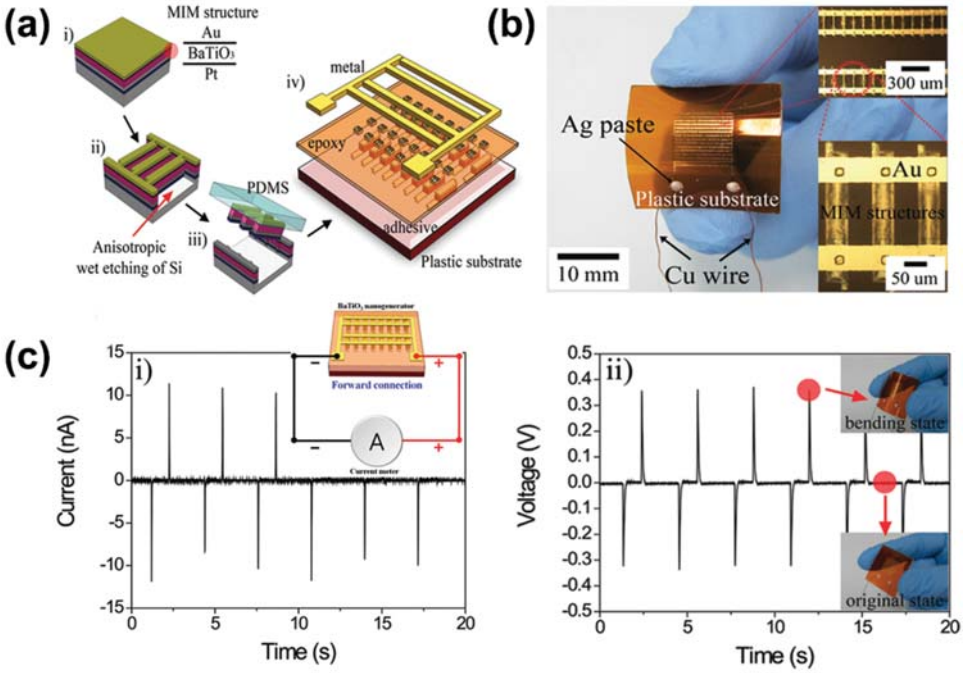

Figure 2. a) A schematic drawing of the fabrication process for flexible $BaTiO_3$ thin-film energy harvester. b) A flexible $BaTiO_3$ NG device supported on PI substrate. The insets show optical magnified images of the MIM structure integrated with metal electrodes. c) The generated output current (i) and output voltage (ii) of the flexible $BaTiO_3$ harvester during motions of bending and unbending. Reproduced with permission.[21] 2010, American Chemical Society.

sapphire substrate by a sol–gel process, followed by high temperature annealing (650 °C). The PZT on a sapphire wafer was then attached onto a receiver PET substrate with an adhesive epoxy. To detach the entire area of the PZT thin film from the mother substrate, an XeCl laser (wavelength of 308 nm) was irradiated to the backside of the sapphire substrate. The XeCl excimer laser beam (photon energy of 4.03 eV) can pass the transparent sapphire (bandgap energy of ≈10 eV) and then partially vaporized the interface between the PZT (bandgap energy of ≈3.4 eV) thin film and sapphire wafer due to high XeCl laser absorption of PZT, thus transferring the PZT thin film from the mother substrate onto the plastic film. This ILLO transfer provided simple, stable, and large-area transfer of high-quality piezoelectric ceramic films annealed at high temperature for self-powered flexible energy sources.[45] After the formation of metal-interdigitated electrodes (IDEs) and a passivation epoxy layer, poling process was performed on the flexible PZT thin film to increase its piezoelectric properties. Figure 3b shows a photograph image of a flexible PZT thin-film harvester on a round glass tube. The PZT energy-harvesting device has outstanding flexibility and mechanical stability during deformation, as shown in the inset of Figure 3b. These benefits were obtained by the optimized ILLO and polymer-coating processes, resulting in high performance of the flexible thin-film harvester. As shown in Figure 3c, when the device was bent by a bending machine, the open-circuit voltage and short-circuit current measured from the thin-film harvester (active area of 1.5 cm × 1.5 cm) were as high as 200 V and 1.5 μA (corresponding to a cross-sectional current density of 150 μA cm^{-2}), representing excellent output performance compared to previously reported piezoelectric energy harvesters on flexible substrates. A flexible large-area PZT thin-film (3.5 cm × 3.5 cm) NG was also fabricated using the ILLO process to increase the electric output energy. Under slight bending motion by fingers, the large-area thin-film harvester generated output voltage of 250 V and output current of 8.7 μA, which were large enough to light 105 blue LEDs without external circuits and energy sources. Figure 3d shows a conceptual illustration of a recently demonstrated self-powered all-flexible light-emitting system based on a flexible piezoelectric thin-film energy harvester and flexible inorganic vertical red LEDs.[38] These works show that a large-area flexible piezoelectric harvester prepared via the dry laser-transfer method can provide sufficient electric power to operate consumer bulk electronics and even flexible optoelectronics.

2.3. Flexible PMN-PT Thin-Film Energy Harvester

Although the previous flexible piezoelectric harvesters successfully operated several consumer electronics, their output current was still low (below 10 μA), thereby restricting the range of applications: for example, an artificial pacemaker needs an input of 3 V and 100 μA.[46,47] Therefore, it is imperative to adopt new flexible materials with high piezoelectric charge constants to increase the output current of piezoelectric energy harvesters. One such material is single crystalline PMN-PT ceramics, which exhibit an extremely high piezoelectric constant (d_{33} of ≈2500 pC N^{-1}) compared to those of conventional piezoelectric materials. Hwang et al. developed a flexible single-crystal PMN-PT thin-film harvester on a thin-plastic substrate

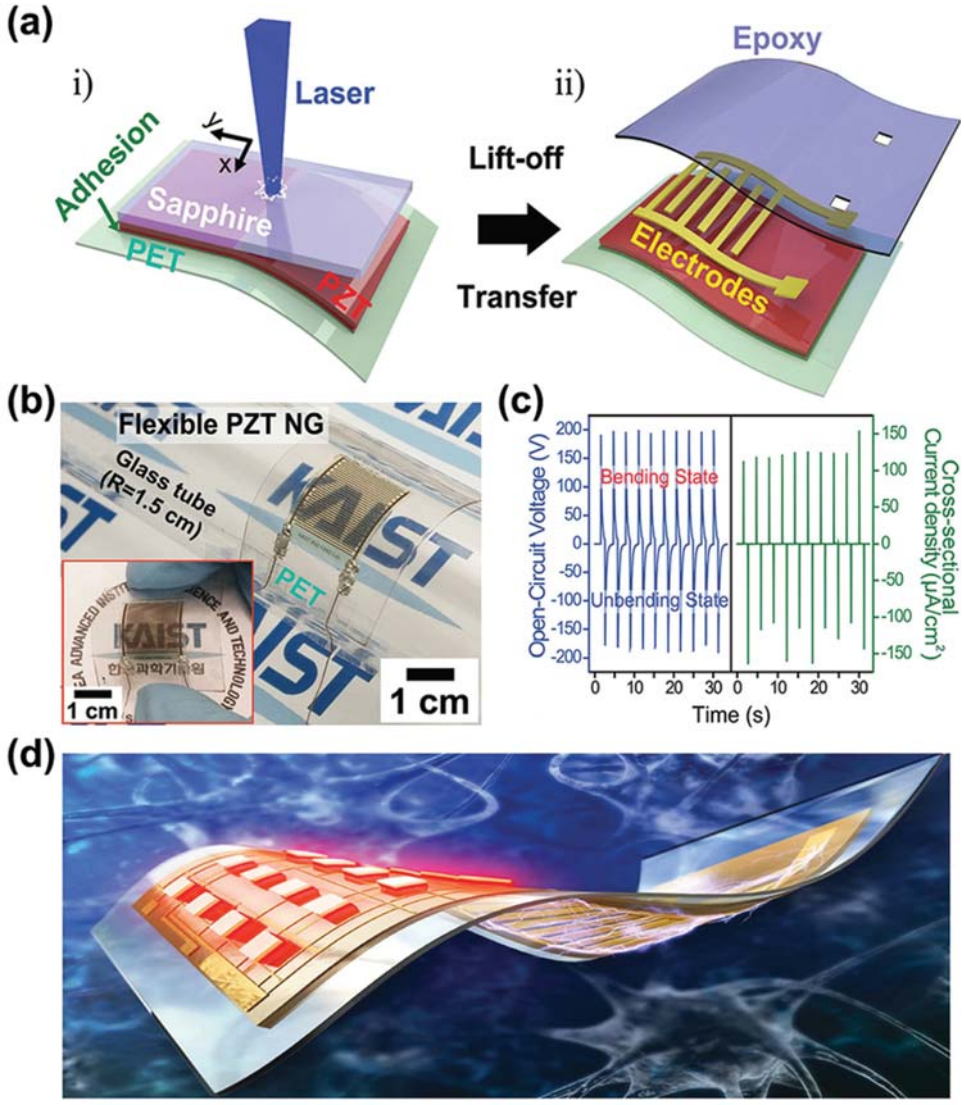

Figure 3. a) A schematic illustration of the fabrication process of the flexible and large-area PZT thin-film harvesting device using the ILLO process. b) The flexible PZT NG attached on a glass tube. The inset presents that the NG device was easily bent by fingers. C) The open-circuit voltage signal and cross-sectional current density generated from the PZT thin-film energy harvester. d) An artistic drawing of self-powered fully flexible light-emitting system combined with flexible thin-film harvester and flexible LEDs on single plastic substrate. Reproduced with permissions.[23,38] Copyright 2014, John Wiley & Sons, Inc. Copyright 2014, Royal Society of Chemistry.

with significantly increased electric output current of up to 0.22 mA, and the current signal from the PMN-PT energy devices was dozens of times higher than that of previously reported piezoelectric NGs on plastic substrates.[48,49] **Figure 4**a illustrates the fabrication procedure of the PMN-PT thin-film NG and a biomedical application as a self-powered cardiac pacemaker. First, a MIM-structured single-crystal PMN-PT thin-film prepared by a modified Bridgman method was situated on an adhesive epoxy-coated Si wafer, and then the piezoelectric thin film was poled by an electric field of 1.8 kV mm^{-1} at room temperature. To transfer the PMN-PT MIM structure onto a plastic substrate, a mechanical exfoliation process using a Ni stress layer was performed. The directional stress mismatch between the thick Ni exfoliation film (tensile stress) and underlying Si wafer (compressive stress) led to spontaneous detachment of the MIM layer from the bulk substrate.[50] This method allowed simple, facile, and precise exfoliation of the piezoelectric large-area thin film (1.7 cm × 1.7 cm) from the rigid substrate without mechanical damage, such as delamination, cracking, or wrinkling.[51] Moreover, this mechanical transfer technology is a cost-effective compared to the large-area transfer of an excimer laser lift-off process. Subsequently, the freestanding Ni/MIM piezoelectric layers were bonded on a PET film by an adhesive polymer, and Ni was etched in a wet etchant to expose the top electrode of the PMN-PT- harvesting device. Lastly, generated power of the PMN-PT thin-film NG was utilized for driving small electronics, and charging batteries. Figure 4b and its inset show an image of the finished flexible PMN-PT thin-film energy harvester. Continual bending and unbending motions of a flexible thin-film NG device yielded an open-circuit output

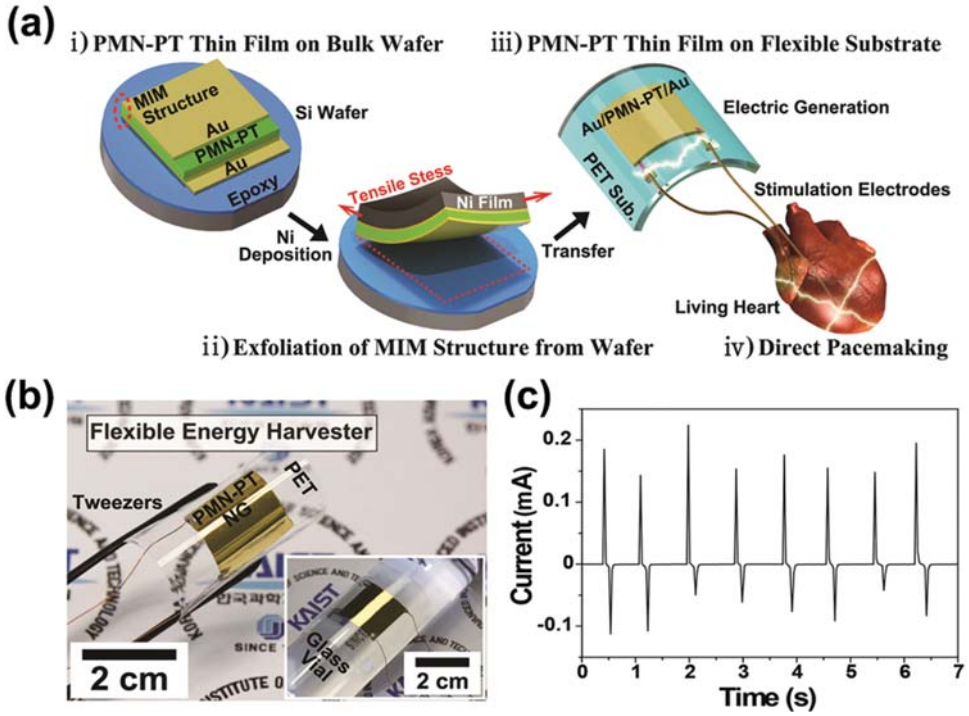

Figure 4. a) A schematic diagram of the fabrication process and biomedical application of PMN-PT thin-film NG. b) The flexible PMN-PT energy harvester on PET substrate bent by tweezers. The inset shows that the NG provided conformal contact with a surface of glass vial. c) Output current from the flexible PMN-PT thin-film device by slight finger tapping. Reproduced with permission.[25] Copyright 2014, John Wiley & Sons, Inc.

voltage signal of 8.2 V and a short-circuit output current signal of 145 μA. Moreover, a huge current output of 0.22 mA was generated by tiny finger tapping from the flexible piezoelectric device, as shown in Figure 4c. As a practical demonstration, 50 parallel-connected LEDs were instantaneously turned on using the high electric output of the PNM-PT NG.

3. Biomedical Applications of Flexible Piezoelectric Thin Films

Flexible piezoelectric thin films are interesting topics in biomedical applications, as researchers seek to exploit the intrinsic piezoelectric characteristic of converting mechanical energy into an electric signal. This section introduces several related biomedical reports such as stimulating heart muscle for artificial pacemaking,[25] sensing small-scale vibration for replacement of damaged sensory organs,[27] harvesting energy from viscera motions for operation of implantable devices,[9] and monitoring cellular deformation[26] using flexible piezoelectric thin films.

3.1. Direct Stimulation of Living Heart

Pulsed electrical signals are widely used to stimulate the heart, specific parts of the brain, and the spinal cord at an in vivo state to cure or ease corresponding illnesses such as abnormal heart rate, Parkinson's disease, and chronic pain.[52] Most implantable biomedical devices provide such functional electrical stimulations for particular muscles and nerves, and in the process generally consume the stored electric energy of embedded batteries.[53] The real-time functional stimulation of living animal muscles and nerves by flexible piezoelectric energy harvesters is highly significant to solve the issues related to deficient energy supply for implantable biomedical devices.[54] Recently, Hwang et al. reported direct stimulation of a heart of a living rat using momentary electric output energy of a flexible PMN-PT thin-film harvesting device without any supplementary power sources.[25] **Figure 5**a presents an experimental schematic illustration of artificial cardiac pacemaking by a PMN-PT energy harvester. In this work, the flexible PMN-PT electric stimulator was connected with metal electrodes to electrically stimulate the living heart of an anesthetized rat, and sensing terminals were attached on the rat body to observe its electrocardiogram (ECG). Figure 5b shows the medical experiment with chest laparotomy of a living rat for generation of an artificial heartbeat. Before the stimulation of the heart, the rat had general P, T waves, and QRS complex in the ECG graph with a regular heart rate of 6 beats per second, as shown in Figure 5c. To trigger the action potential for artificially stimulating the living heart, electric power of a few μJ is commonly required for various animals including humans.[55] When the flexible PMN-PT thin-film energy harvester was periodically bent and released, corresponding tall and sharp peaks were recorded for the natural heartbeat of the rat in the ECG, as displayed in Figure 5d. The PMN-PT harvester generated electric energy of 2.7 μJ, which was large enough to electrically excite the rat heart as an artificial heart stimulator. This approach verified that the flexible PMN-PT thin-film stimulator mounted on thin plastics has

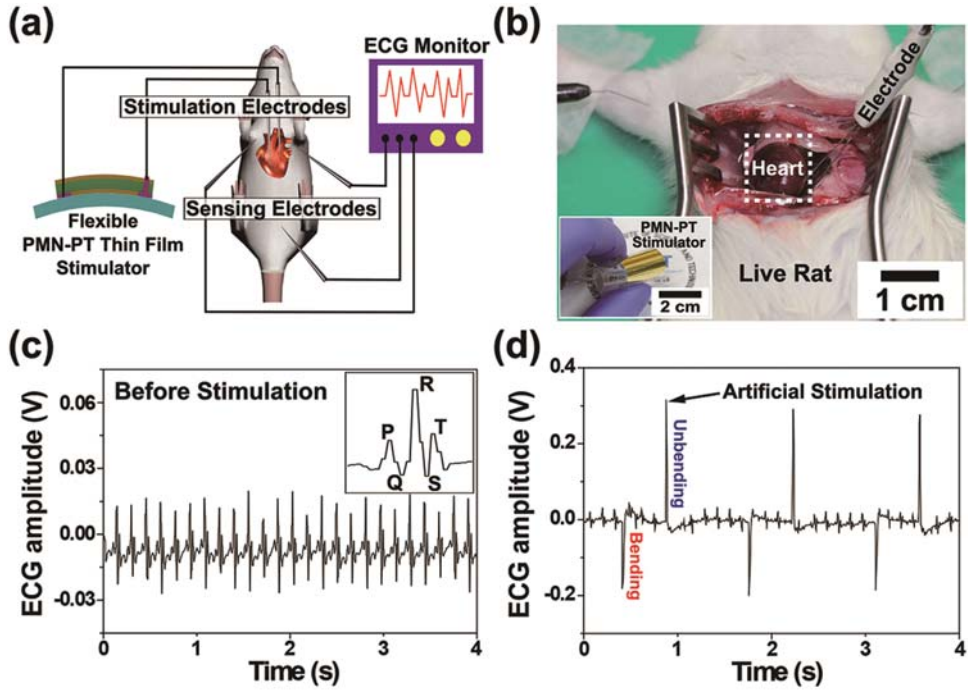

Figure 5. a) A schematic of the experimental setup for artificial cardiac pacemaking using the electric output from the flexible PMN-PT thin-film NG. b) A real image of the animal experiment on a rat to stimulate the living heart. The inset shows a photograph of flexible PMN-PT heart stimulator. c) The measured ECG of the rodent before the artificial excitation. The inset presents typical P wave, T wave, and QRS complex of the heart beating. d) Artificial heart beats on ECG made by periodic motions of bending and unbending of the flexible PMN-PT thin-film device. Reproduced with permission.[25] Copyright 2014, John Wiley & Sons, Inc.

strong potential for biomedical applications including normalization of heart beating and brain stimulation for treatment of movement disorders.[54,56]

3.2. Acoustic Sensor for Biomimetic Artificial Hair Cell

The flexible piezoelectric thin films can also serve to restore lost human sensory organs by using their sensitive conversion of tiny mechanical stress into electricity. For example, a research group attempted to restore sensorineural hearing loss, which is caused by damage of hair cells in a cochlea, through the adoption of a polyvinylidene fluoride (PVDF) membrane to mimic the role of auditory hair cells.[57] The PVDF material was placed on the basilar membrane (BM) of the cochlea to detect vibration of the BM in response to sound waves and transduce the stimulation into electric energy. Although the PVDF has the benefit of flexibility originating from the polymer-based material, utilizing inorganic piezoelectric ceramics with high piezoelectric charge coefficients can be advantageous to directly stimulate the cochlear nerve.[58] Recently, Lee et al. reported an inorganic piezoelectric acoustic nanosensor (iPANS) utilizing flexible PZT thin films for biomimetic artificial hair cells. A flexible PZT thin-film nanosensor on PET film was fabricated by the ILLO process.[23] **Figure 6**a presents a conceptual illustration of the organ of Corti and the flexible PZT thin-film beneath the BM to respond to sound stimulation. In the organ of Corti, the inner and outer hair cells are located normal to the BM. When a sound wave causes vibration of the BM, the hair cells generate electricity by oscillatory motion, whereas the sound can be transmitted to the brain. To replace the natural function of damaged hair cells, the piezoelectric PZT thin films could sensitively produce an electric signal in the organ of Corti, responding to the tiny vibration of the BM. The theoretical simulation proved that the PZT thin film as an artificial hair cell under the BM can generate piezoelectric potential of 3 V in response to horizontal BM displacement of 600 nm by a general acoustic wave, which may be sufficient voltage to directly stimulate the auditory nerve.[57] In a similar protocol experiment, acoustic nanosensors of three flexible IDE-type PZT thin films were attached on an artificial trapezoidal silicone BM to mimic the natural hair cells. Figure 6b shows a schematic drawing of an oscillating silicone-based BM in response to produced white sound noise (frequency range of 3.125 Hz to 20 kHz and 40 dB of sound pressure). Figure 6c provides a photo image of the silicone BM with a-, b-, and c-PZT nanosensors arrayed at the apex, intermediate, and base area of silicone BM, respectively. The inset of Figure 6c presents a flexible PZT device on a round glass stick, showing mechanical flexibility of the iPANS. When a sound wave was applied to the silicone BM, the freestanding silicone membrane oscillated due to the resonant effect. The vibration motion of the trapezoidal artificial BM near the apex of the silicone membrane can be amplified by relatively low-frequency sound, while its motion near the base of the silicone membrane can be amplified by relatively high-frequency sound due to the difference of membrane width.[59] Therefore the three PZT thin-film nanosensors on the distinguished sites of the artificial BM were deformed maximally by

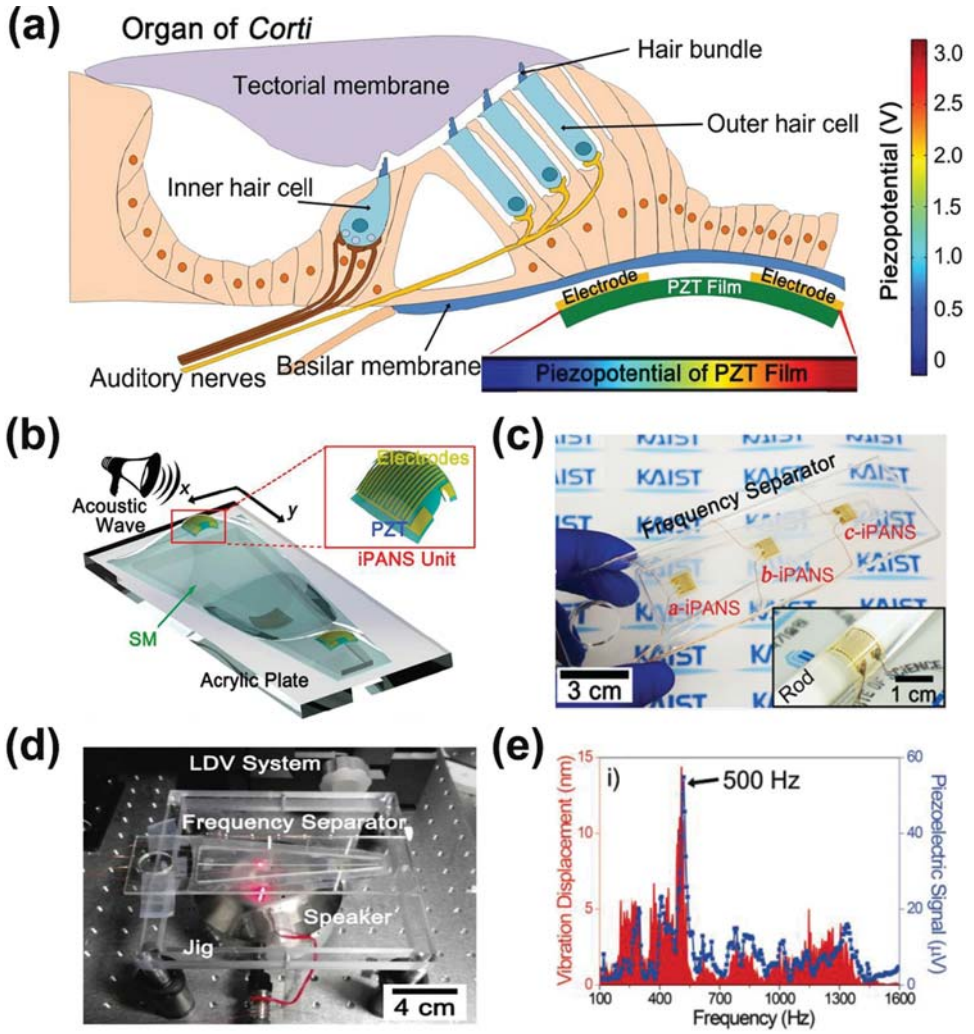

Figure 6. a) A conceptual illustration of organ of Corti in mammalian cochlea. The PZT thin film placed under BM can generate electric potential of ≈3 V by vibration of BM. b) The silicone BM was vibrated by sound wave, resulting in mechanical deformation of PZT thin films on the artificial BM. c) The completed iPANS units on the frequency separator. The inset shows PZT thin-film device on a glass rod. d) An experimental setting for measuring vibration displacement of the silicone membrane in response to the acoustic wave. e) A vibration amplitude and a piezopotential generated by a-iPANS recorded by LDV and a sound level analyzer in the frequency of 100 Hz–1600 Hz. Reproduced with permission.[27] Copyright 2014, John Wiley & Sons, Inc.

a specific sound frequency in a region and they yielded electric potential from the PZT material. Figure 6d shows an image of the experimental setup for measuring the oscillatory property of the silicone membrane as a frequency separator. The vibration displacement of the artificial BM was recorded by a laser Doppler vibrometer (LDV) and a sound-level analyzer. Figure 6e shows the oscillatory displacement of the apex region of the silicone BM and the corresponding piezoelectric output voltage of the PZT nanosensor located on the apex site of the membrane. The incoming sound frequency of 500 Hz maximized the vibrational displacement (14.4 nm) of the silicone membrane near top resonance point, which was related with transducing mechanical vibration into piezopotential voltage (54.8 μV) of the flexible thin-film acoustic nanosensor. The artificial BM and iPANS units at the different areas of the middle and bottom of the silicone membrane also successfully distinguished other representative frequency points of 600 Hz and 1000 Hz within the audible frequency range, respectively. These results can be extended to develop an implantable iPANS system with suitable electric output for directly stimulating the auditory nerves and realizing fully implantable artificial hair cells.

3.3. Harvesting Energy from Motions of Organs

Harvesting energy from natural movement/pressure inside the human body potentially offers an attractive solution for future bio-implantable devices.[56] In particular, motions of the heart and lung provide an inexhaustible source of mechanical energy throughout human lifetime. Flexible piezoelectric materials can provide a feasible route to transduce these biomechanical energies into electric power. In 2010, a flexible piezoelectric harvester based on ZnO nanowires was applied to in vivo self-powered harvesting from the movements of a rat's diaphragm/heart,

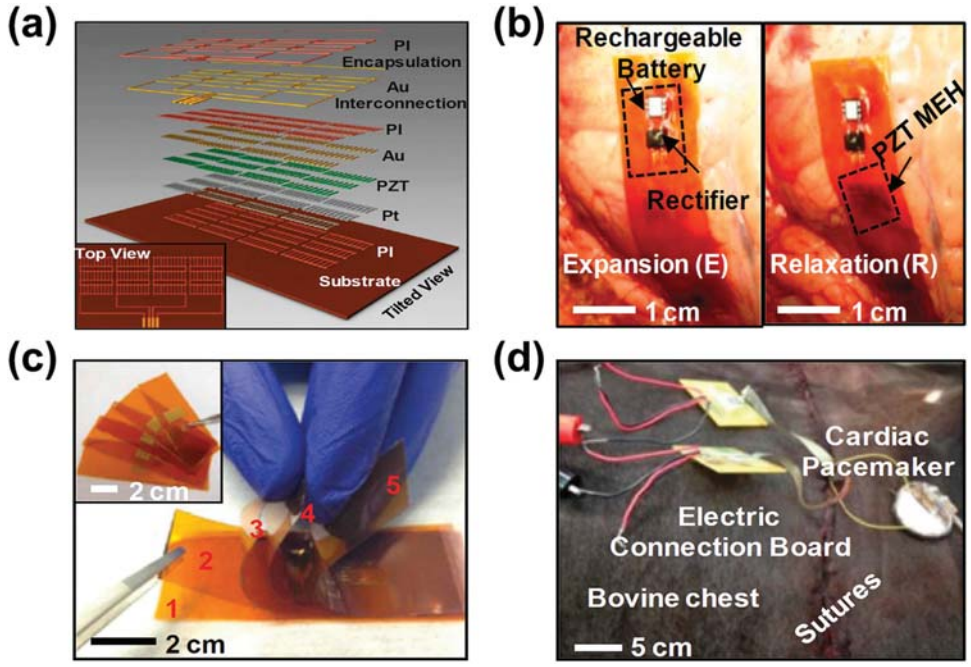

Figure 7. a) An expanded schematic illustration of the flexible PZT energy harvester with the top view (inset). b) The flexible thin-film NG integrated with micro-secondary battery and rectifier, attached on the right ventricle of a bovine heart during a cycle of expansion (left) and relaxation (right). c) A multilayer stack of five flexible PZT thin ribbon devices in series connection. The inset shows five independent PZT energy harvesters before stacking process. d) A photograph of an in vivo PZT thin-film harvester connected with rectifier, battery, and pacemaker on a bovine heart. Reproduced with permission.[9] Copyright 2014, National Academy of Sciences.

but the output signals of ≈1 mV and ≈1 pA were extremely low.[60] Dagdeviren et al. reported an in vivo flexible piezoelectric energy harvester and storage system using the movements of the heart, lung, and diaphragm.[9] **Figure 7**a presents schematic diagrams of a flexible PZT thin-film NG by a similar process of the above-mentioned wet- etching protocol.[21] The flexible PZT mechanical harvester with biocompatible encapsulation layer can be integrated with a bridge rectifier and a micro battery on a plastic substrate to capture energy directly from bovine heart movement (Figure 7b). During cardiac motions of contraction/relaxation, the flexible energy harvester and storage system maintained conformal contact on the heart without any destruction. The in vivo energy harvester attached on the right ventricle (RV) of a bovine heart yielded open-circuit voltage of 3 to 5 V from movements of the organ. This suggests strong feasibility to supply self-powered electric energy for implantable biomedical devices. Figure 7c provides an interesting demonstration of an in vivo energy-harvesting system, implanted in a closed chest with an external artificial cardiac pacemaker. Figure 7d shows an image of a multilayer-stacked flexible NG composed of five independent PZT harvesters with a serial connection. The multilayer flexible PZT energy harvesters generated a voltage signal of 8.1 V, which was much larger than that of the single-layer generator, and the power density of device is as large as 1.2 μW cm^{-2}.[61]

3.4. Monitoring Cellular Deformation

Examining mechanical reactions of cells by means of electric activation can allow us to effectively understand cellular physiology and biology.[62,63] Although the electric reactions of neurons with induced voltage have been intensively investigated, their mechanical response to electric stimulation is not well known yet.[64] Nguyen et al. reported freestanding PZT nanoribbons for monitoring micro- and macro-cellular deflections to overcome the drawbacks of conventional AFM methods.[26] Highly piezoelectric PZT thin films were utilized to maximize the electromechanical effect for detecting cellular deformations on a nanometer scale. **Figure 8**a schematically illustrates a PZT nanoribbon with cultured neuronal cells. The freestanding nanoribbons were fabricated by partially removing the sacrificial MgO substrate. PC12 cells from the pheochromocytoma of rat adrenal medulla were cultured on the freestanding part of piezoelectric nanoribbons, and those cells were patch-clamped with a glass pipette electrode for membrane voltage excitation. Figure 8b shows a scanning electron microscopy (SEM) image of a single PC12 cell directly interfaced with suspended PZT nanomembranes. To measure the mechanical deflection of PC12 cells, the cells on a PZT ribbon array were stimulated by membrane voltage, resulting in variation of cellular volume. Figure 8c shows that distinguishable output signals (blue line) from suspended PZT nanoribbons were recorded simultaneously with the deformation of PC12 cells stimulated by applied membrane voltage (green line). They can quantitatively relate between the alternation of membrane voltage and the cellular force (Figure 8d) based on AFM measurement of PZT sensitivity (Figure 8e). A membrane voltage change of 120 mV induced a cellular force of 1.6 nN on the freestanding PZT thin films. From the result, they inferred that cellular deformation of 0.5 nm influenced a single PZT ribbon. This study could provide a novel

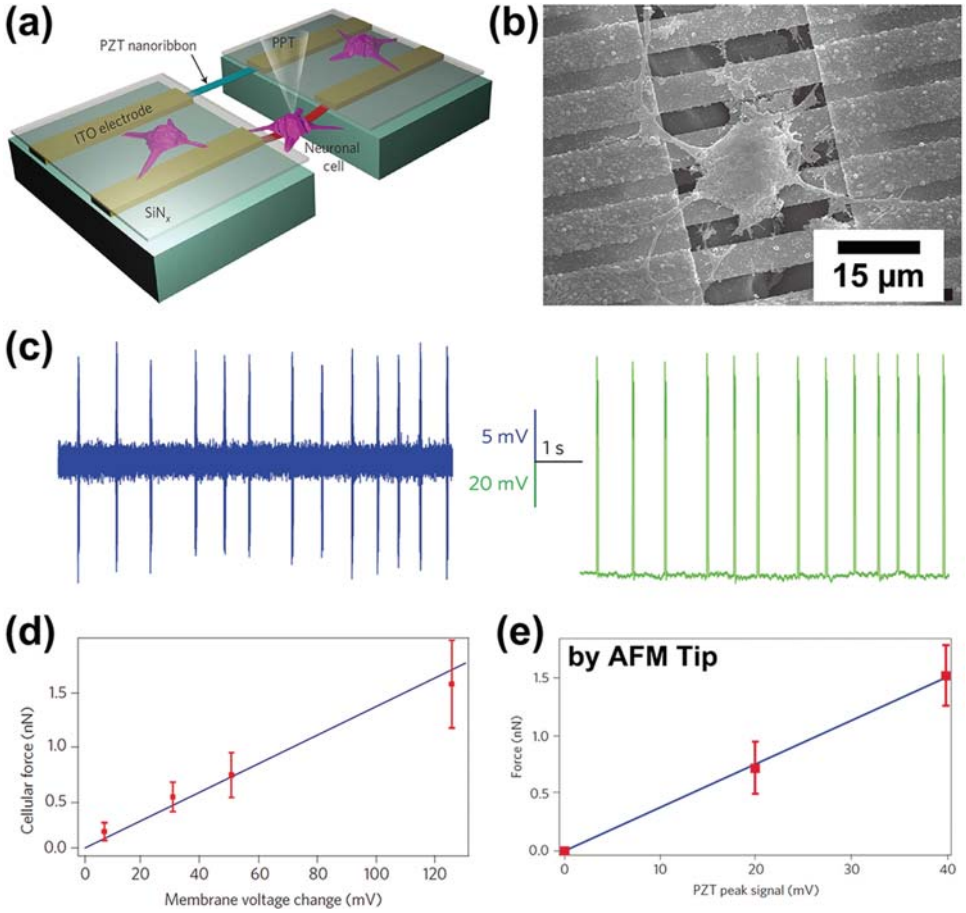

Figure 8. a) A schematic illustration of the freestanding PZT nanoribbons directly interfaced with neuronal cells. The PZT ribbons record cellular mechanical deformation while the standard glass electrode applies and records membrane voltage. b) A SEM image of a PC12 cell cultured on the suspended PZT thin films. c) Response of PZT nanomembranes (blue line) to cellular deflections derived by applied membrane potential (green line). d) The relationship between applied cellular force and membrane voltage change. e) A graph of the electric signal of piezoelectric nanoribbons and the imparted force from the AFM tip. Reproduced with permission.[26] Copyright 2012, Macmillan Publishers Limited.

biorecording system from the small signals of cells and neurons such as dendrites and axons, and synaptic boutons.

4. Biomedical Self-Powered Flexible Systems

Flexible piezoelectric thin films can be utilized as a sustainable energy source and nanosensor in a biomedical self-powered flexible system.[65] **Figure 9**a illustrates a conceptual drawing of such a system on a heart, integration of a piezoelectric thin-film energy harvester, a thin-film battery, large-scale integration (LSI), and biosensors on a single flexible substrate. The implantable self-powered electronics have comprehensive multifunction of energy harvesting/storage, data processing, information memory, wireless communication, and medical diagnosis/treatment in a human body.[9,16] Recently, related remarkable flexible electronic technology including a flexible secondary battery (Figure 9b), flexible LSI (Figure 9c), and flexible diagnosis/therapy device has developed, allowing the realization of a self-powered flexible biomedical system.[66,67]

Koo et al. reported a high-performance flexible thin-film lithium-ion battery (f-LIB) by using physical delamination of a sacrificial substrate, to utilize a high temperature (up to 700 °C) annealed $LiCoO_2$ cathode on a polymer sheet. The flexible battery had a high energy density of 2200 μWh cm^{-3} with an output voltage of 4.2 V, which enabled an all-in-one flexible light-emitting system combined with a flexible energy source. Hwang et al. demonstrated a silicon-based flexible LSI (f-LSI), composed of thousand CMOS nanotransistors for in vivo radio frequency (RF) applications. Flexible LSI has been a long-term goal for logic operation of the main process unit (MPU), high capacity memory, and wireless communication on plastics. In the report, a 0.18 μm CMOS RF-integrated circuit (IC) was transferred from a silicon-on-insulator onto a plastic substrate with elimination of the entire bottom silicon wafer. The flexible RFICs exhibited an effective transistor mobility of 400 cm^2 V^{-1} s^{-1} and high-performance RF-switching properties. Son et al. presented a wearable and stretchable diagnosis/therapy device for treating movement disorders of Parkinson's disease by integrating flexible drug delivery.[68] This patch-type flexible biomedical system is composed of nonvolatile memory, drug release actuator, and physiological biosensors, allowing the record of muscle activity/body temperature on epidermis and the subcutaneous delivery of therapeutic drugs.

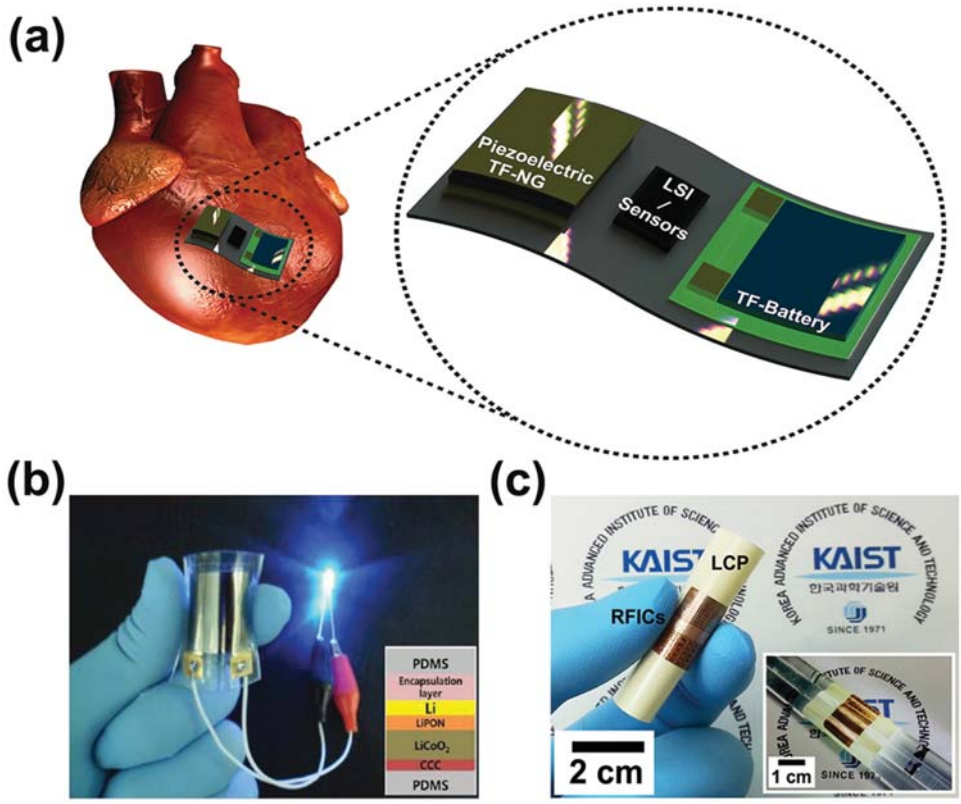

Figure 9. a) A conceptual schematic of biomedical self-powered flexible system including piezoelectric thin-film (TF)-NG, sensors, LSI, and TF-battery on a heart. b) A photograph of flexible TF lithium ion battery (LIB) and its structure (the inset). c) Images of flexible radio frequency integrated circuits (RFICs) on a plastic substrate. Reproduced with permissions.[16,69] Copyright 2012, 2013, American Chemical Society.

5. Conclusion

This paper has described several exciting flexible piezoelectric thin films that have been developed for energy harvesters and nanosensors in biomedical applications. The flexible piezoelectric thin films afford the benefit of converting slight movement into an electric signal, and thus can be used as power generators or sensitive mechanical nanosensors. In particular, piezoelectric thin-film harvesters with high piezoelectric constants of PZT and PMN-PT have yielded dramatic enhancement of electric output power for flexible energy harvesters. The electric power harvested from the bending motion of a flexible thin film was sufficient to stimulate heart muscle. Moreover, the flexible piezoelectric thin film can generate meaningful electric energy from tiny movements of internal organs. This technical development may extend the flexible thin-film harvesters as a permanent energy source in in vivo self-powered biomedical devices to substitute or support conventional embedded batteries. **Figure 10** gives a summary on the performance improvement

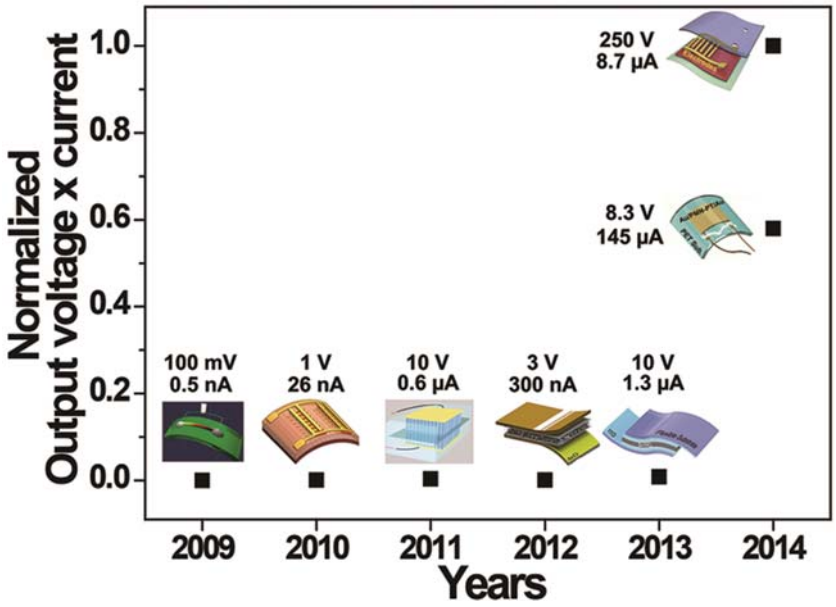

Figure 10. A summary on the performance improvement of flexible piezoelectric energy harvesters since 2009. The normalized products of generated open-circuit voltage and short-circuit current by bending motions were used to compare the performance of flexible piezoelectric NGs. Reproduced with permissions.[10,33,70,71] Copyright 2009, 2010, 2011, American Chemical Society. Copyright 2013, 2014, John Wiley & Sons, Inc.

of flexible piezoelectric energy harvesters since 2009. The normalized products of generated open-circuit voltage and short-circuit current by bending motions were used to compare the performance of flexible piezoelectric NGs. Note that energy the conversion efficiency of flexible thin-film NG on a single plastic substrate is higher than nanocomposite-type generator of two sandwiched flexible substrates due to easy bendability. As mechanical nanosensors, flexible piezoelectric thin films also show very sensitive sensing capability, even permitting detection of nanoscale deformations. This flexible thin film can be used as a replacement of damaged hair cells in the cochlea by transmitting electric signals scavenged from acoustic vibration. In addition, freestanding piezoelectric nanoribbons can record cellular deformation by measuring small volume changes of neurons and cells. These nanosensors demonstrate that flexible piezoelectric materials can provide a novel and distinct platform for biomechanical monitoring systems. Lastly, high-performance flexible piezoelectric thin-film technologies will open up a key role in the development of biomedical self-powered system that has functions of self-energy generation, real-time diagnosis/therapy, and RF communication. The flexible and freestanding piezoelectric thin films could also apply to various industrial applications such as extremely sensitive actuators and sound/ultrasonic transducers.

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