Emerging Pyroelectric Nanogenerators to Convert Thermal Energy into Electrical Energy

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Pyroelectric energy harvesting systems have recently received substantial attention for their potential applications as power generators. In particular, the pyroelectric effect, which converts thermal energy into electrical energy, has been utilized as an infrared (IR) sensor, but upcoming sensor technology that requires a miniscule amount of power is able to utilize pyroelectric nanogenerators (PyNGs) as a power source. Herein, an overview of the progress in the development of PyNGs for an energy harvesting system that uses environmental or artificial energies such as the sun, body heat, and heaters, is provided. It begins with a brief introduction of the pyroelectric effect, and various polymer and ceramic materials based PyNGs are reviewed in detail. Various approaches for developing polymer-based PyNGs and various ceramic materials–based PyNGs are summarized in particular. Finally, challenges and perspectives regarding the PyNGs are described.

1. Introduction

The conversion of environmental energy into electrical energy has recently become a research topic of interest on the self-powering internet of things systems (IoTs).[19–23] However, due to energy limitations, IoTs require astronomical budgets for constant maintenance, such as battery replacement and power construction.[7,8] If a temporary power source is used, it will require periodic replacement of the battery, which causes an enormous waste of resources.[9–11] In addition, it is difficult to directly connect power cables with tremendous sensors, so a wireless energy transfer function or a self-powering function is necessary for the sustainable operation of IoTs.[12] Though ultralow power consumption technology can extend the operation time of IoTs, it is still not a permanent solution for persistent operation.[13] Therefore, converting wasted environmental energy into valuable electricity is one of the important technologies for a self-powering IoTs.[14–18]

Among the various energy harvesting systems,[19–23] converting thermal energy into electric energy is a recently emerging technology.[24–31] Unlike other energy converting systems, the pyroelectric effect, which converts thermal energy into electric energy, has been used as a sensor due to its sensitive responsiveness to temperature fluctuations. However, increasing output performance of the pyroelectric nanogenerators (PyNGs) and decreasing power consumption of IoTs have begun a paradigm shift of pyroelectric devices from sensors to power sources. In addition, the PyNGs are easily hybridized with other energy harvesting systems, such as piezoelectric and triboelectric NGs (TENGs) which are recently developed energy harvesters[32–39] to enhance the output performance.[40] Piezoelectric and triboelectric NG convert external mechanical energy into electrical energy using piezoelectric effect and triboelectric effect, respectively. Thus, thermal energy which is generated by nature, mechanical friction, and machines, can be effectively converted into electric energy through the pyroelectric effect, and it can be utilized as new type power sources of IoTs.

As shown in Figure 1a, pyroelectric applications such as heat sensors, infra-red (IR) sensors, thermal imaging, fire alarms, gas analyzers, and pollution monitors have been continuously developed and utilized since the pyroelectric effect was introduced.[41–44] Recently, pyroelectric energy harvesting systems have emerged as new applications of the pyroelectric effect, and research on PyNGs has gradually increased. Typical PyNGs comprise three layers: the patterned top metal layer is designed to receive heat energy efficiently, and also acts as a top electrode; the middle pyroelectric layer converts thermal energy into electric energy through changing its internal polarization; and the bottom metal layer acts as a bottom electrode (Figure 1b). Due to the simple structures of the PyNGs, pyroelectric material design and structure design are key factors for enhancing the output performance. For example, there are several approaches to enhance the output performance of the PyNGs, such as increasing thermal energy absorption by structure modification, increasing the pyroelectric coefficient by material modification, or enhancing internal polarization change by thermal expansion. Therefore, in this review paper, we will discuss the working principle of the PyNGs as well as detailed overview of polymer-based PyNGs and ceramic based-PyNGs.

2. The Pyroelectric Effect

Pyroelectric materials have internal spontaneous polarization ($P_s$) in the absence of an electric field and pyroelectric effect is temporary change of $P_s$ by the temporal temperature change.
of pyroelectric materials.\cite{42} When the temperature increases, decreasing $P_s$ by thermal vibration leads to a decrease of surface charges bound to the surface.\cite{42} If the pyroelectric material is under open circuit condition, electrical potential is generated across the material.\cite{45} If the pyroelectric material is under short circuit condition, electrical current flows through external circuit. Theoretical short circuit output current is defined as follows in Equation (1)

$$i = \frac{dQ}{dt} = pA \frac{dT}{dt}$$

(1)

where $i$ is generated current, $Q$ is pyroelectric charge, $p$ is the pyroelectric coefficient, $A$ is surface area of pyroelectric material, and $t$ is time. The unclamped material's pyroelectric coefficient under constant stress and electric field is expressed by following Equation (2)

$$p^{\sigma,E} = \left( \frac{dP_s}{dT} \right)^{\sigma,E}$$

(2)

where subscripts $\sigma$ and $E$ correspond to constant stress and electric field, respectively. Though the pyroelectric coefficient is vector quantity, the measured pyroelectric coefficient is often treated as a scalar quantity.\cite{46} In order to precise quantification of pyroelectric coefficient, several methods are introduced under static and dynamic conditions.\cite{46} Static condition methods are 1) charge compensation method, 2) hysteresis measurement method, 3) direct electrocaloric measurement, 4) flat band-voltage shift, 5) X-ray photoelectron spectroscopy (XPS) method, and 6) X-ray diffraction (XRD) and density functional theory. Dynamic condition methods are 1) temperature ramping methods, 2) optical methods, 3) periodic pulse technique, 4) laser intensity modulation methods, and 5) harmonic waveform techniques. Although these are very precise analysis methods to evaluate pyroelectric materials, complicated device structures and input environmental conditions interfere their pyroelectric output performance. Thus, reflecting output current and physical parameters of PyNG is more useful for evaluating practical pyroelectric coefficient of PyNG, whose pyroelectric coefficient is calculated by followed Equation (3)

$$p = \frac{i}{A \cdot dT/dt}$$

(3)

As shown in Figure 2a–c, schematic images show the working principle of the PyNG based on temperature change induced $P_s$ change.\cite{47} For example, crystalline polymers with aligned molecular chains can have $P_s$ due to the alignment of polarized covalent bonds and ionically bonded ceramic

![Figure 1. a) Time sequence of relevant articles on pyroelectrics and pyroelectric nanogenerators in Scopus. b) Schematic illustration of energy harvesting system based on pyroelectric effect.](image)
materials can also have $P_s$ due to the polarization of crystal structure.**41** Ideally, all internal dipoles formed by $P_s$ would align along one direction, but wiggling atoms disturb the perfect dipole alignment. Under invariable temperature condition, $P_s$ and wiggling angle ($\theta$) are constant, and there is no current flow through external circuit (Figure 2a). When the temperature increases ($dT/dt > 0$), thermal energy change dipole alignment, which wiggle around their respective pole axes (Figure 2b). Thus, diverse polarizations have larger wiggling angles ($\theta_1 > \theta$) at higher temperatures, significantly decreasing the intensity of $P_s$. Thus, induced surface charges on pyroelectric material are reduced and released surface charges flow through the external circuit. When the temperature recovers to its original status, the dipole alignment of pyroelectric material is recovered, so increasing surface charges induce reverse current flows through the external circuit. Conversely, when the temperature decreases ($dT/dt < 0$), internal dipoles have smaller angles ($\theta_2 < \theta$) due to reduced thermal energy, which significantly increases the intensity of $P_s$ (Figure 2c). Thus, induced surface charges on pyroelectric material are increased and induced surface charges flow through the external circuit. When the temperature recovers to its original status, the dipole alignment of pyroelectric material is recovered, so decreasing surface charges induce reverse current flows through external circuit. Therefore, temperature change induced internal polarization change generates electrical energy based on the pyroelectric effect.

The $P_s$ change of pyroelectric materials dependent on temperature is shown in Figure 2d.**30** The $P_s$ decreases with different polarization change rate while increasing the temperature of material. When the pyroelectric material reaches the Curie temperature ($T_C$), the $P_s$ rapidly decreases to zero, but the pyroelectric coefficient rises significantly. Though pyroelectric material loses its pyroelectric property above the $T_C$, strong polarization change beneath the $T_C$ of the material will be effective for pyroelectric energy harvesting. Working temperature condition controls will increase the pyroelectric coefficient of the materials, which is able to dramatically increase output current of PyNGs.

### 3. Polymer Based Pyroelectric Nanogenerators

**3.1. PyNGs Driven by Various Environmental Conditions**

Ferroelectric materials such as lead zirconate titanate (PZT), barium titanate (BTO), polyvinylidene fluoride (PVDF), and poly(vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE)] that maintain spontaneous polarization have both pyroelectric and piezoelectric property and have utilized for IR sensor, actuator, and energy harvester. Polymer-based pyroelectric nanogenerators mainly utilize ferroelectric polymers, which are PVDF and P(VDF-TrFE). Despite the low pyroelectric coefficient of PVDF, PVDF has high mechanical flexibility and biocompatibility, which applicable to wearable devices.**45** Leng et al. reported a high performance PVDF based PyNG with simple Cu/PVDF/Cu structure using hot and cold water as a thermal energy source (Figure 3a).**47** In order to prevent oxidation and conductivity by water, 30 µm thick polyvinyl chloride (PVC) thin film covered the device. The device was evaluated by alternating contact with the hot flow (40, 60, 80 °C) and cold flow (0 °C). As the hot flow temperature increased, the output performance of the PyNG increased from 6 to 11 µA. In addition, they mechanically deformed the PyNG to enhance the internal polarization change at varying temperature. The output performance of the thermal expanding/shrinking induced mechanical deformed PyNG was dramatically enhanced, which were around 100 to 190 V
while hot water temperature changed from 40 to 80 °C. At the optimum external load resistance, the maximum output power reached 126 µW. To understand high output voltage of the PyNG, finite element method (FEM) simulation was performed using COMSOL Multiphysics software. The pyroelectric coefficient of PVDF film was 2.7 nC cm⁻² K⁻¹.[41] The simulated electrical potential distribution of cross-sectional PVDF film was maximum 774 V, which was higher than the experiment results due to partial contact with the flows and heat loss from the PVC thin film. For the actual usage of the PyNG, they operated 42 light emitting diodes (LEDs) and charged a 100 µF capacitor.

Zabek et al. demonstrated a PVDF based flexible PyNG with micropatterned top electrode layer in order to enhance heat transfer and to achieve larger temperature fluctuations (Figure 3b).[48] Partially covered micropatterned top electrode was exposed to an IR radiation as a heat source, which was largely absorbed wavelength of PVDF.[49] The partially covered aluminium (Al) electrodes with 10 × 10 µm² square array on flexible PVDF film. In order to evaluate PyNGs, a 175 W IR light bulb placed on 15 cm upper than the samples and heated the samples up from room temperature. The PVDF based PyNGs showed different temperature profiles depending on the electrode coverage (100%, 88%, 70%, 53%, 45%, 28%, and 19%), which resulted in 45% and 53% coverage devices showing about 30% larger temperature change than the others. This large temperature changes led faster rates of change in temperature and led to 400% higher voltage and current output performance. Therefore, balanced design between current collector and exposed PVDF area was able to maximize their energy conversion efficiency without complicate development.

Gao et al. reported P(VDF-TrFE) base high performance PyNGs driven by hot water vapor to utilize fast temperature oscillation (Figure 3c).[50] Water is a perfect heat transfer medium due to its ability to absorb and release a large amount of heat through evaporation and vapor condensation on a surface. A large flexible thin film PyNG was fabricated by polyimide (PI) tape sealed PVDF and P(VDF-TrFE). Water vapor was supplied by continuous evaporation from hot water and the PyNG evaluated at room temperature with less than 50% relative humidity (RH) condition. In order to create an oscillating airflow like environment, a mini-fan was used to produce a 1–2 m s⁻¹ oscillating flow. Hot water vapor condensed to form microscale water droplets on the surface of PyNG, and released heat to the PyNG. When the PyNG was exposed to airflow, the local humidity near the PyNG was decreased and microscale water droplets were quickly evaporated with absorbing heat of the PyNG. The IR camera measured the PyNG and hot source temperature, which the PyNG heated up around 65 °C by hot water vapor and quickly cooled down to 40 °C by air flow. This observation demonstrated that water vapor was able to efficiently heat up and cool down, and the PyNG harvested peak voltage of 160 V and peak current of 5.5 µA using the thermal energy of water vapor. The maximum power output of the PyNG was 220 µW at optimum resistance, and it successfully demonstrated charging of a 2.2 µF capacitor, operating a digital watch, and turning on blue LEDs.

Raouadi and Touayar described pyroelectric effect base wind energy harvesting using wind turbulence and vortex generator
They inserted a vortex generator in the flow passage to enhance the convective heat transfer between a PyNG and wind, and they designed wind tunnel for accurate measurement of a PVDF based PyNG. When air flow passed through the vortex generator, turbulences were created with changing temperatures and physical properties of flow. Viscous stresses which were proportional to the gradient of the velocity and heat fluxes were proportional to the temperature gradient. Additionally, heat transfer was occurred by turbulence heat fluxes. Thus, the PyNG was able to generate energy without interruption. A number of output signals were strongly related with flow velocity, and peak output voltage of the PyNG also increased with increasing flow velocity. The maximum power of the wind driven PyNG was 2.8 $\mu$W cm$^{-2}$ at optimum load resistance, and it was able to operate a white LED and sound buzzer.

3.2. Development of Pyroelectric Materials

Polymer based flexible and thin PyNGs have been used to harvest thermal energy at various environmental conditions with a variety of structures. However, due to the limitation of pyroelectric coefficient, output performance of PyNGs is not dramatically enhanced. In order to overcome the low pyroelectric coefficient, several approaches have been reported such as crystallinity control for enhancing the pyroelectric coefficient, strain coupling effect, and polymer modification. Kim et al. reported that high dipole moment solvents controlled the crystallinity of P(VDF-TrFE) to enhance the pyroelectric coefficient (Figure 4a).\[52\] Dipole moment of tetrahydrofuran (THF), methyl ethyl ketone (MEK), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) is 1.75, 2.7, 3.8, and 4.1 D, respectively. Dissolved P(VDF-TrFE) in four different solvents were examined their crystallinity by XRD and differential scanning calorimetry (DSC) measurements. Gel permeation chromatography (GPC) measurements were performed to measure the relative chain length of P(VDF-TrFE). A high dipole moment solvent based P(VDF-TrFE) thin film had small full width at half maximum (FWHM) value of $\beta$ ferroelectric phase\[53\] and DSC result showed that high dipole moment solvent-based P(VDF-TrFE) had the highest crystallinity than other samples. High crystallinity
of P(VDF-TrFE) was mainly due to long end-to-end chain length of P(VDF-TrFE). GPC measurement also confirmed high dipole moment solvent-based P(VDF-TrFE) had a high molecular weight. High crystalline P(VDF-TrFE) had a higher degree of dipole alignment and pyroelectric coefficient than low crystalline P(VDF-TrFE) which result in 1.4 times higher output peak voltage and current. Therefore, higher dipole moment solvent offered promising strategy to increase pyroelectric coefficient of P(VDF-TrFE) and power performance of P(VDF-TrFE) based PyNGs.

Lee et al. introduced stretchable PyNGs and thermally induced strain coupling effect in order to enhance output performance of PyNG using P(VDF-TrFE) and polydimethylsiloxane (PDMS) (Figure 4b). Micropatterned PDMS was able to be utilized as stretchable substrate for PyNG and its high thermal expansion coefficient than P(VDF-TrFE) was able to induce compress force to P(VDF-TrFE) while heating. They confirmed the β ferroelectric phase of patterned P(VDF-TrFE) by Fourier transform infrared (FT-IR) and XRD spectroscopy. Different thermal expansion coefficient of neighbored two materials built thermal expansion induced strain, so specially designed PDMS provided additional strain to P(VDF-TrFE) during heat. Internal polarity of the P(VDF-TrFE) was changed by heat and strain, which result in five times enhanced pyroelectric output performance by same temperature changing condition. In addition, the low thermal conductivity of PDMS remained higher heat in P(VDF-TrFE) than the high thermal conductivity substrate device. Thus, large thermal expansion of PDMS induced huge compressive strain into P(VDF-TrFE), which generated a larger negative potential by coupling negative piezoelectric and negative pyroelectric potential. They also demonstrated that the PDMS based PyNG was able to stretch over 15% without output degradation and operated red, yellow, and green LEDs and black liquid crystal display (LCD). Micropatterned substrate based the stretchable and strain coupled PyNG offered efficient strategy to enhance output performance and stretchability of polymer based PyNG.

Ghosh et al. reported Er 3+ modified PVDF (Er-PVDF) film based enhanced pyroelectric property through the formation of a self-polarized ferroelectric β phase and porous structure (Figure 4c). Similar additives such as Ce 3+, Eu 3+ and Yb 3+ also have a self-polarized ferroelectric β phase and have been explored to enhance the piezoelectric properties of PVDF, but integrated PVDF and Er 3+ design enhances thermal sensitivity under an IR irradiation due to superior optical activity of Er 3+. When Er-salt was mixed with PVDF-DMF solution, Er 3+ was presented in Er-PVDF that was confirmed by XPS. The strong O−H bond of water and F−C bond of PVDF drove the −CH2−CF2 dipoles so Er-PVDF dipole was self-polarized ferroelectric β phase with high thermal stability than bare PVDF. Er-salt created porous structure of PVDF with a flower like surface morphology due to fast crystallization, so it was highly flexible compared to thin PVDF film. Due to Er 3+, Er-PVDF film was a good IR absorber. Thus, small-scale energy was efficiently converted into electric energy by pyroelectric effect. When temperature change rate was less than 1 K s⁻¹, peak current of output was 13 nA. Using the PyNG, it was successfully charged a 4.7 µF capacitor to operate the low power consumer electronics. Therefore, in order to enhance the PVDF property, IR sensitive Er 3+ modification was one of the promising methods.

3.3. Wearable Pyroelectric Nanogenerators

Human is one of the abundant thermal energy sources, so PyNGs are able to use power source of wearable electronics. To utilize PyNGs as wearable device, flexibility, stretchability, or fiber type materials are required. Xue et al. reported integrated a N95 respirator and a PVDF thin film PyNG for harvesting energy of human respiration (Figure 5a). They demonstrated self-powered breathing sensor using a flexible PVDF film installed on a common respirator for sustainable energy harvesting and self-powered breathing monitoring. The size of 3.5 cm × 3.5 cm PVDF thin film with thickness of 30 µm was exposed by the body exhaled gas that had the same temperature of body. The temperature-changing rate of the PyNG by human exhaled gas was 13°C s⁻¹ and the corresponding peak output current and voltage of the PyNG was 2.5 µA and 42 V, respectively. The maximum output performance of the PyNG was 8.31 µW at the load resistance of 50 MΩ, and the PyNG showed stable output performance after ten days without power degradation. The water vapor accompanied from exhaled gas was able to condense on the PyNG, which resulted in an increasing temperature quickly, but decreasing temperature slowly. In order to demonstrate a sustainable capacitor charging by exhaled gas, a simple circuit using a 10 µF capacitor and a rectifier was designed for energy harvester. The PyNG successfully charged a capacitor to 1 V in 18 s and turned LEDs and LCD on.

Although PVDF thin film is able to be used as a wearable device, fiber type PVDF is required to overcome the limitation of the flexibility and stretchability of thin film PVDF. Mokhtari et al. introduced an electrospinning method to make PVDF nanofibers (Figure 5b). Electrospinning at low temperature of chamber or quick evaporation of solvent formed the β ferroelectric phase of PVDF without post treatment, but the mechanical force by rotating was not effective in forming the β ferroelectric phase. A high voltage was applied in order to eject the PVDF solution at a controlled flow rate. An electrostatic force from a high voltage overcame the surface tension of the PVDF solution at the needle of electrospinning equipment. The charged fluid jet was collected on ground due to electric field between the PVDF solution and ground. The whipping motion of the PVDF jet allowed the solvent evaporation, so the β ferroelectric phase PVDF nanofibers were collected on the collection plate. The distance between the tip and the collection plate was one of the key factors to control the diameter of PVDF nanofiber. In order to analyze PVDF nanofibers, FT-IR, XRD, and DSC analysis were performed and proved the β ferroelectric phase. Therefore, the electrospinning method is able to make the β phase PVDF nanofibers and fabric without additional poling process for wearable energy harvesters.

3.4. Wearable Pyroelectric Nanogenerators

In order to realize the stretchable hybrid PyNGs for wearable electronic devices, Lee et al. reported patterned PDMS-carbon nanotubes (CNTs) composite and graphene nanosheets based highly stretchable PyNGs (Figure 6). Graphene, which had high thermal conductivity and flexibility was used as top electrode instead of metal electrode. To fabricate the stretchable hybrid PyNG, patterned PDMS-CNT composite for stretchable
substrate was obtained using silicon (Si) master mold. P(VDF-TrFE) was spin coated on the micropatterned PDMS-CNT directly, and annealed at 140 °C for 2 h. XRD and FT-IR analysis were confirmed the β ferroelectric phase of P(VDF-TrFE). Lastly, multilayer graphene was transferred on the P(VDF-TrFE). Due to patterned CNT-PDMS, P(VDF-TrFE) and graphene followed the pattern of CNT-PDMS, which result in increasing stretchability of P(VDF-TrFE) and graphene electrode than flat P(VDF-TrFE) and graphene. Human body was able to apply mechanical deformation and temperature change on the hybrid PyNG. Thus, both piezoelectric and pyroelectric effect occurred in P(VDF-TrFE), which resulted in both piezoelectric and pyroelectric output being generated.

Piezoelectric and pyroelectric effects both changed internal polarization of P(VDF-TrFE) by external force and temperature change, respectively. Stretching and releasing of P(VDF-TrFE) made opposite internal polarization change, and heating and cooling also made opposite internal polarization change. Thus, mechanical change and temperature change were able to reinforce internal polarization change with proper environment change. For example, releasing and heating the device enhanced internal polarization change in P(VDF-TrFE), or compress and heating the device enhanced internal polarization change in P(VDF-TrFE). Piezoelectric peak output voltage of the hybrid PyNG was 1 V, and pyroelectric peak output voltage of the Hybrid PyNG was 0.4 V. The hybrid PyNG output peak voltage was increased up to 1.4 V under mechanical deformation and temperature change, which was similar with summation of each piezoelectric and pyroelectric output voltage. They demonstrated that the stable output performance of the hybrid PyNG depends on the stretch rate and mechanical durability after 30% stretching. Thus, patterned substrate is able to provide stretchability to nonstretchable P(VDF-TrFE) and graphene for wearable application.

3.5. Hybrid Pyroelectric Nanogenerators

Hybridization of the various energy harvesting systems is an effective strategy for enhancing the energy conversion efficiency, thus hybrid pyroelectric, piezoelectric, triboelectric, and photovoltaic energy harvesters are used for high performance energy harvesting systems. In order to hybridize different energy harvesting systems, impedance of each energy harvesting system is matched, or energy harvesters with different impedance use temporary energy storage such as capacitor, battery to coordinate different energy harvesters in one device. Thus, similar impedance-based hybrid nanogenerators are not required special electrical connection, but different impedance-based hybrid nanogenerators are required for power management circuit or impedance matching. You et al. demonstrated PVDF based piezoelectric and pyroelectric hybrid nanogenerator (PPNG) (Figure 7). They reported a lightweight and flexible hybrid nanogenerator using PVDF nanofiber.

Figure 5. Wearable PyNGs using polymer material. a) Real photo and schematic images of the wearable PyNG. Reproduced with permission.[69] Copyright 2017, Elsevier Ltd. b) Schematic image of electrospinning process and SEM images of fibrous PVDF. Reproduced with permission.[70] Copyright Taylor & Francis.
membrane (NFM) without post poling treatment. A thermoplastic polyurethane (TPU), carbon nanotube slurry (CNTS), PVDF, and PEDOT:PSS-polyvinyl pyrrolidone (PVP) conductive NFM (CNFM) were sequentially deposited by electrospinning process. The morphologies of the NFMs were characterized using a scanning electron microscope (SEM) and XRD. The conductivity of CNTs layer was about $4.4 \times 10^{-3}$ S cm$^{-1}$, and the conductivity of CNFM was about $1.27 \times 10^{-4}$ S cm$^{-1}$. Due to the electrospinning process, both electrodes showed outstanding flexibility, thus, they were suitable for wearable applications. The hybrid NG that the effective size was 4 cm $\times$ 4 cm generated 2.85 $\mu$J at 3 Hz impact-release cycle. Due to the time-dependent piezoelectric output performance, output performance of the hybrid NG was increasing with increasing impact force and speed. Pyroelectric output performance of the hybrid NG was about 20 nA small temperature change condition, and piezo-pyroelectric output performance of the hybrid NG was successfully summation due to enhanced spontaneous polarization change. They demonstrated a walking-based energy harvesting system and arm bending based energy harvesting system for wearable applications. When the device was under mechanical deformation and temperature change, both piezoelectric output and pyroelectric output were successfully integrated to generate a hybrid output.

Integrated with another energy harvesting system is a practical approach for increasing the power performance of an energy harvester. In particular, TENGs have simple structures for generating displacement current to convert mechanical energy into electric energy. Sun et al. reported one structure flexible and biocompatible tribo/piezo/pyroelectric hybrid NG with transparent electrodes (Figure 8a).[75] The hybrid NG consisted of PDMS, PVDF and silver (Ag) nanowires which were favorable in terms of mass production and the hybrid NG had 82% transmission due to high transparency of each component. Replicated leaf-venation (LV) pattern mould was utilized to enhance conductivity with high transparency of electrodes. To harvest mechanical energy, finger pressing the PDMS generated surface triboelectric charge on PDMS and internal polarization change of PVDF. Induced current flows between top and bottom transparent electrodes by triboelectric charge and internal dipole change generated 55 V and pyroelectric effect induced current flows generated 86 V. They demonstrated potential flexible smart wearable sensors using the hybrid NGs. Wrist, throat, and neck attached the hybrid NG successfully demonstrated heartbeat, swallowing, neck tilting and coughing sensors. They inserted LCD film between electrode and PDMS to demonstrate temperature gradient of human finger, so the color of LCD changed from black to red, green, and blue depend on the temperature change rates by finger touch. They also demonstrated breath sensor that was able to distinguish weak, normal, and deep breath depend on the pyroelectric output performance driven change of LCD color display.

Another reported tribo/piezo/pyroelectric hybrid NG by Zhang et al. was used as both a thermal and mechanical energy harvester, and for electromagnetic shielding purposes using PVDF, Ag, and rubber (Figure 8b).[76] Decreasing electromagnetic radiation is important for preventing potential threats to human health, and thus they presented a new type wearable hybrid NG included wide electromagnetic shielding range. The developed stretchable and wearable electromagnetic shielding hybrid NG (ES-HNG) was composed of a stretchable TENG and several piezo/pyro hybrid NGs. The TENG was composed of a layer of conductive anti-electromagnetic radiation fabric and rubber. Owing to the island structure of the ES-HNG, it had
40% stretchability with slight change. The mechanical deformation of the ES-HNG generated triboelectric and piezoelectric potential with excellent strain sensitivity and pyroelectric potential was formed by temperature change. The hybrid piezoelectric NG (PENG) and TENG generated peak output current of 6 nA at applied 0.3 N force condition and 18 nA at bending condition. The PyNG generated peak output current of 15 nA at small temperature change. They fabricated keyboard cover using ES-HNG to harvest biomechanical energy and to decrease electromagnetic radiation. It successfully harvested 20 µA, charged a 10 µF capacitor, and decreased electromagnetic radiation from 6261 to 0 µW cm$^{-2}$. They also demonstrated self-powered health monitor and wide range electromagnetic radiation protector for pregnant woman. This interesting demonstration of energy harvester-based electromagnetic radiation protecting material suggests future smart functional energy harvesters.

Zheng et al. designed individually/simultaneously harvesting thermal energy and wind energy using hybrid TENG, PENG and PyNG (Figure 8c). A PPNG that used polarized PVDF thin film deposited by Cu electrodes was capsulated by PI tape to prevent water vapor contamination. Fluorinated ethylene propylene (FEP) film was applied to cover the PVDF film for triboelectrification layer. One end of the PPNG flutter was fixed on the side of Cu deposited substrate and the other side of the PPNG was left free. During the contact and separation process between Cu electrode and FEP film by wind, periodic alternative output was generated by TENG, which peak output voltage and current were 350 V and 30 µA, respectively. Temperature change and mechanical deformation of the flutter formed piezoelectric potential and pyroelectric effects induced internal polarization change of PVDF. Peak output voltage of the PENG was 20 V, and peak output voltage and current of PPNG that was enlarged output due to enhanced polarization change was 350 V and 41 µA, respectively. They demonstrated charging a 22 µF capacitor with various combinations of TENG, PENG, and PyNG. TENG and PPNG hybrid generator charged three to five times faster than individual NGs, and it successfully turned...
on 24 small white LEDs and turned on 31 green LEDs using human breath.

Zhang et al. demonstrated a flexible PPNG using a polarized PVDF film so as to scavenge both thermal and mechanical energies (Figure 8d)[80]. An inductively coupled plasma-driven reactive ion etching was performed for enhancing a TENG performance to modify surface morphology of the polytetrafluoroethylene (PTFE) film.[81] In order to harvest mechanical energy based on triboelectrification and electrostatic induction, the Al top and bottom electrodes deposited PVDF film of the PPNG had contact with a surface modified PTFE film to generate large triboelectric charges; peak output voltage and current of the TENG were 8 V and 420 nA, respectively. The PVDF base PyNG was evaluated under 3.2 K s\(^{-1}\) temperature change rate; peak output voltage and current of the PyNG were 3.2 V and 100 nA, respectively. The PVDF base PyNG was evaluated under 3.2 K s\(^{-1}\) temperature change rate; peak output voltage and current of the PyNG were 3.2 V and 100 nA. The PENG generated peak output of 2.3 V and 30 nA when a compress force was applied. When various energy sources applied to the hybrid NG, output performance of each NG was coupled to each other and successfully turned up a LCD by hand touch. Another practical application of the hybrid NG was self-powered cathodic protection (CP). Electrochemical impedance spectroscopy analysis was performed in order to analyze their electrochemical characteristics. The corrosive property of steel with and without CP showed that the hybrid NG decreased polarization potential and corrosion rate.

Conventional TENGs and PENGs waste thermal energy that is converted from mechanical energy by friction heat, but Zi et al. reported triboelectric–piezoelectric–pyroelectric hybrid high efficient NG to utilize mechanical energy and friction induced heat energy (Figure 8e).[82] The mechanical energy of sliding and pressing was harvested by TENG and PENG and friction induced heat energy was converted into electricity by PyNG. The TENG was consisted of Al foil as the sliding part and PTFE film deposited Cu electrode as the static part. The PPNG were consisted of Cu deposited PVDF film and PI film was laminated between TENG and PPNG to prevent electric shortage. When Al foil slide on the hybrid NG, sliding motion induced surface triboelectric charge change and press force induced internal polarization change of PVDF generated current flow through external circuit. Friction induced heat also induced internal polarization change of PVDF by pyroelectric effect and generated current flow. Peak output voltage and current of TENG was 1132 V and 1.45 mA m\(^{-2}\), respectively, and maximum peak power was 146 mW m\(^{-2}\) at the matched load of 140 M\(\Omega\). The output voltage and current of PPNG was 3 V and 6 \(\mu\)A, respectively. They successfully demonstrated that it could power up a LED bulb and charge a 41.9 mF capacitor. A self-powered sensor of the temperature and the normal force was also demonstrated using a modified hybrid NG structure. It was able to measure at least 0.09 °C change and 0.5 N force.

Wang et al. demonstrated another one structure based tribo-piezo-pyroelectric hybrid NGs using large-scale PVDF (Figure 8f).[83] PVDF nanowires, PDMS, indium tin oxide (ITO) electrodes were used for transparent, flexible, and hybridized
NG. Ferroelectric $\beta$ phase of PVDF nanowire fabricated by electro-spinning process having diameters of 200 to 500 nm was confirmed by XRD analysis.\cite{84,85} The total transparent of the device was exceeding 95% and 30 cm x 30 cm sized PVDF and PDMS composite film was fabricated for large-scaled NG.\cite{86} A flexible nylon film was contacted and separated with PVDF-PDMS composite film to make contact electrification and strain in PVDF-PDMS composite. When 15 m s$^{-1}$ speed of airflow was applied to the device, TENG and PENG part of the device-generated peak current and voltage output of 20 $\mu$A and 0.6 V under 400 k$\Omega$, respectively. The PyNG part of the device generated a peak current and voltage of 120 nA and 120 V, respectively, and maximum output power was 6.05 $\mu$W under a load resistance of 1.5 G$\Omega$. For the application, the hybrid NG successfully turned on two light bulbs and charged a 10 $\mu$F capacitor under various conditions. Therefore, polymer based transparent and flexible hybrid NGs are able to harvest mechanical and thermal energy efficiently for wearable sensor and power source.

In order to enhance the output power of the TENG and PENG, integration of solar cell and PPNG was introduced by Yang et al. (Figure 9a).\cite{87} PVDF was used as a PPNG and zinc oxide (ZnO) nanowires grown on flexible polyester and poly(3-hexylthiophene) (P3HT) heterojunction solar cell were used as a solar cell. The bottom PPNG consisted of Ag electrode and PVDF film. The top solar cell consisted of ITO transparent electrode, ZnO nanowire array, P3HT film, and Ag electrode. When temperature change rate was 0.8 K s$^{-1}$, the PyNG harvested 2.5 V and 2.4 nA, and the pyroelectric coefficient of PVDF was $-44$ $\mu$C m$^{-2}$ K$^{-1}$, which was larger than ZnO and KNbO$_3$.\cite{88,89} When a compress force was applied on the PENG, peak output voltage and current were 0.5 V and 20 nA, respectively. Using the PPNG, they demonstrated the derivation of a LCD by human touch. In order to harvest solar energy, ZnO nanowire-P3HT cell was evaluated under air mass (AM) 1.5 illumination light intensity; open circuit voltage of the solar cell was 0.4 V and short circuit current of solar cell was 31 $\mu$A cm$^{-2}$. When the solar cell

![Figure 9. Solar, mechanical and thermal hybrid NGs. a) Schematic image of ZnO nanowires and PVDF-based solar and thermal hybrid NG. Reproduced with permission. Copyright 2012, American Chemical Society. b) Schematic image of P(VDF-TrFE), DSSC, and thermoelectric hybrid NG. Reproduced with permission. Copyright 2015, American Chemical Society.](image-url)
and PyNG were simultaneously operated, both output performances were successfully integrated and enhanced. The PPNG and solar cell hybrid nanogenerator successfully charged a Li-ion battery and charged battery turned on four red LEDs.

Another solar cell, pyroelectric, and thermoelectric hybrid system was introduced by Park et al. for enhancing power performance of polymer based nanogenerator (Figure 9b).[90] PEDOT film, P(VDF-TrFE) film, titanium dioxide (TiO2) based dye sensitized solar cell (DSSC) and thermoelectric devices were used as a hybrid nanogenerator. Major challenge of the hybrid nanogenerator was high photothermal (PT) effect, transparency, electrical conductivity, and surface energy matching of the PEDOT film. PEDOT was coated on both sides of β phase P(VDF-TrFE) through the solution casting polymerization used as PyNG part.[91,92] It is abbreviated as PP-PEDOT hereafter. Compare the PT effect of bare PVDF and the PP-PEDOT by near infrared (NIR) irradiation, the PP-PEDOT showed higher PT effect with the greatest temperature change (ΔT > 10 °C). The PyNG generated peak voltage and power under NIR irradiation were 0.2 V and 22 µW m−2, respectively. For an efficient heat transfer, a thermal paste was coated on the thermoelectric device; output voltage and current of thermoelectric device were 11 mV and 13.6 mA, respectively, which was five times higher voltage output than previous reports.[93,94] Due to absorption wavelength of DSSC, from 400 to 1600 nm range of the light was able to transmit DSSC and absorbed by the PP-PEDOT. Thus, the DSSC, the PyNG, and thermoelectric device all efficiently harvested light energy. The energy conversion efficiency of the DSSC under AM 1.5 illumination light intensity was 9.72% and the energy conversion efficiency of the hybrid NG was 11.7% with increasing open circuit voltage. Using the voltage enhanced hybrid NG, they successfully demonstrated that it could charge a 47 µF capacitor and operate a white LED as well as an electrochromic display by light. Therefore, hybridization of energy harvesting systems is able to enhance output performance of NGs, but enhancing pyroelectric coefficient is demanded for higher energy conversion efficiency and simplification of NGs.

4. Ceramic Based Pyroelectric Nanogenerators

4.1. ZnO Based Pyroelectric Nanogenerator

Ceramic based pyroelectric materials such as ZnO, PZT, KNbO3, 1,4-diazabicyclo[2.2.2]octane perrenenate (dabcHReO3), BiFeO3 (BFO), and BTO have higher pyroelectric coefficient and stronger thermal shocks than the polymer pyroelectric materials that are described above. Thus, ceramic material based PyNGs have been utilized for high-resolution thermal sensor applications. Yang et al. reported ZnO nanowire arrays based pyroelectric nanogenerator (Figure 10a).[98] ZnO nanowires were grown on the ITO substrate and Ag was deposited on the ZnO as the top electrode in order to make Schottky contact with ZnO. Temperature fluctuation created the anisotropic polarization in ZnO nanowires, which resulted in electron flow through external circuit.[99] I–V characteristic of the PyNG confirmed a Schottky contact between ZnO nanowires and Ag. Under 0.5 K s−1 temperature change rate condition, the PyNG generated peak output voltage and current of 5.8 mV and 108 pA, respectively. Output performance of the PyNG was linearly increasing with increasing the temperature change rate in the device. Pyroelectric coefficient of the ZnO nanowires was 1.2–1.5 nC cm−2 K−1 that was larger than previous reports due to c-axis oriented ZnO structure.[92,90] COMSOL multiphysics simulation of electrical potential distribution in a single ZnO nanowire was shown from −3.1 to 2.6 V, which was larger than the experimental results due to screening effect of the free charge carriers.[97,98]

Another wurtzite ZnO nanowire based PT triggered flexible PyNG and self-powered photosensor were reported by Wang et al. (Figure 10b).[99] Wurtzite crystal structure of ZnO nanowires that used as pyroelectric material was effectively tuned the charge transport across the p–n junction by pyroelectric potential. The variation of the depletion region was caused by built-in potential change, which resulted in the expansion of shrinkage of the depletion region. The NIR light triggered PyNG modified p–n junction of Si/ZnO nanowires for self-powered photodetector. Si p-type semiconductor and ZnO n-type semiconductor formed depletion region at the junction interface. With NIR irradiation, the pyroelectric potential was created within ZnO nanowires and induced electron flow through an external circuit. The depletion width was also expanded by change of electric field inside a ZnO nanowire. When NIR irradiation was shut down, a reverse pyroelectric potential occurred in the ZnO nanowire, which resulted in shrinking the depletion width and reverse current flow through an external circuit. Peak current of the PyNG was 2 µA at the NIR light irradiation condition. Under strong NIR irradiation condition, peak current of the PyNG was 1 mA and on/off photocurrent ratio was up to 107.

4.2. PZT Based Pyroelectric Nanogenerator

Yang et al. reported a PZT film based PyNG with a high pyroelectric coefficient and self-powered nanosystems (Figure 11a).[100] A 175 µm thickness of PZT film was deposited on a 300 nm thick nickel (Ni) and top electrode of Ni was deposited on the PZT film. Peak output voltage and current of the PyNG was 2.8 V and 42 nA, respectively, at temperature change of 0.2 K s−1 condition. Obtained pyroelectric coefficient of PZT film was 80 nC cm−2 K−1 which was much larger than that of ZnO.[88,97] At higher temperature change rate condition, the PyNG generated peak voltage of 22 V, peak current of 430 nA, and corresponding maximum peak power of 0.2 mW cm−3. The PyNG was able to be continuously driven for longer than 60 s, which was 30 times higher performance than previously reported PENG.[101] Compared with COMSOL simulation results and experimental result, the PyNG required a lot of enhancement before it could reach the theoretical value. The PyNG was used to charge a Li-ion battery for a practical application. The battery was charged by the PyNG from 650 to 810 mV in 3 h, and total stored capacity was 23 nAh.

PZT micro/nanowire based PyNG was reported to detect the temperature of a fingertip by Yang et al. (Figure 11b).[102] A PZT micro/nanowire was achieved by pressing of a bulk PZT, and a PZT micro/nanowire was poled by applied voltage of 3.5 kV. Two ends of a PZT microwire were fixed by Ag paste on glass.
substrate, and PDMS layer was covered on the device to avoid atmosphere, contamination, and corrosive effect. Peak output voltage and current of the PyNG was 60 mV and 0.6 nA under 1.5 K s\(^{-1}\) temperature change condition, respectively. In order to utilize the PyNG as a sensor application, the PyNG was attached on the metallic body and contact/separate with heat source. The response time of the PyNG was 0.9 s, and the decay time of temperature response was 3 s. The PyNG was evaluated under different temperatures conditions of heat source. It was able to expect that output voltage increased with an increasing heat source temperature. The linear relationship indicated good performance for temperature sensor and linear change of the output voltage was good to calibrate temperature change rate.

Ko et al. reported a flexible PENG and PyNG hybrid energy harvester using PZT film to harvest mechanical and thermal energies in extreme conditions (Figure 11c).\(^{[103]}\) PZT film was fabricated by spin coated method on a flexible LaNiO\(_3\)/Ni-chromium substrate, and platinum electrode was deposited on the PZT film. In order to align the ferroelectric polarization of the PZT film, they applied 20 V for 30 min, and the mechanical property of the PZT film was evaluated by XRD and Raman scattering measurements. The obtained a flexible PZT film's piezoelectric coefficient was 157 pC N\(^{-1}\) and pyroelectric coefficient was 50 nC cm\(^{-2}\) K\(^{-1}\), which was comparable to the reported papers.\(^{[104,105]}\) While the hybrid NG was touched, the temperature change was 1.5 K with the rate of 1 K s\(^{-1}\). Peak output voltage and current of the PyNG was 0.05 V and 0.1 \(\mu\)A cm\(^{-2}\), respectively. Peak output voltage and current of the PENG was 0.3 V and 0.3 \(\mu\)A cm\(^{-2}\), respectively under 0.4% strain condition. The hybrid NG generated peak voltage and current of 0.34 V and 0.34 \(\mu\)A cm\(^{-2}\), respectively. Output performance of the wind driven hybrid NG was almost linearly increased with wind velocity and temperature change rate. They demonstrated a highly durable property at harsh environmental conditions at highly humid and strong base conditions. Output performance

Figure 10. ZnO-based PyNGs. a) SEM and schematic images of the ZnO-based PyNG. Reproduced with permission.\(^{[88]}\) Copyright 2012, American Chemical Society. b) Schematic image of the ZnO-based PyNG and self-powered photodetector. Reproduced with permission.\(^{[99]}\) Copyright 2017, American Chemical Society.
of the hybrid NG maintained their output performance at RH of 70% and pH of 13. When ultraviolet (UV) was exposed on the hybrid NG, output performance of the PENG was decreased by 24%, but output performance of the PyNG was maintained. Thus, PZT is a good candidate for energy harvesters to operate at harsh conditions.

Another PZT-based hybrid NG for self-powered electrocatalytic oxidation was reported by Yang et al. (Figure 11d).[106] Simultaneously/individually mechanical and thermal energy harvesting for a self-powered electrodegradation of methyl orange was fabricated by PZT based PyNG and PDMS based TENG. A flexible PDMS nanowire array was used as triboelectric material and PZT film was used as pyroelectric material. Peak output voltage and current of the TENG was 12 V and 0.2 µA, respectively, and peak output current of the PyNG was 0.3 µA. Harvested energy by the hybrid NG was stored in a Li-ion battery from 0.18 to 1 V and then stored energy was used for the electrodegradation of MO. Absorption peak change of MO showed decreased MO concentration, and the color of the MO solution was changed from red to yellow. They also demonstrated MO electrodegradation through direct powering of the hybrid NG.

Zhang et al. demonstrated simultaneously scavenging environmental energy by piezo–tribo–pyro–photoelectric effect coupled NG (Figure 11e).[107] Integration of a PyNG, solar cell, TENG, and PENG into one device was able to efficiently harvest ambient energy. PZT block was used as active material of piezoelectric, pyroelectric, and photoelectric; polyamide was used as flexible vibrating film for triboelectric material and applied strain to PZT; Ag, ITO, and Ag nanowire imbedded PDMS film were used as electrodes; thermoelectric module was integrated to convert thermal energy into electric energy. Due to one structure and same output electrodes, simultaneous or individual outputs were integrated. The PyNG generated peak voltage and current of 100 V and 480 nA, respectively. The solar cell generated voltage and current of 60 V and 890 nA with the illumination-induced heat effect, respectively, but the solar cell without the illumination-induced heat effect generated voltage and current of 48 V and 170 nA, respectively. The TENG and PENG hybrid NG generated a peak current of 3.8 µA under an airflow speed of 15 m s⁻¹, but the voltage was not measurable. When all energy harvesting systems harvest energy, they were able to provide a charge of 71 µC. For practical application, they charged a 10 µF capacitor to 5.1 V in 90 s. Therefore, one structure based on various integrated energy harvesting systems realizes maximizing energy scavenging from environment.

### 4.3. Lead-Free Ceramic Based Pyroelectric Nanogenerator

In order to achieve wearable PyNG applications, the nontoxic property of pyroelectric materials is crucial for biocompatibility. Thus, PZT-based PyNGs have high output performance, but the development of lead-free pyroelectric materials is inevitably required. Yang et al. reported a single crystalline lead-free KNbO₃ nanowire based PyNG (Figure 12).[89] The KNbO₃ nanowires were synthesized by hydrothermal process. For flexible
property of the PyNG, PDMS and KNbO3 nanowires were mixed with volume ratio of 7:3. Mixed PDMS was spin coated on ITO substrate and Ag was deposited as a top electrode. A transmission electron microscopy (TEM) measurement and corresponding selected area electron diffraction (SAED) pattern analysis confirmed the phase of the perovskite structure. In the combined SAED patterns and HR-TEM image, the crystal direction of nanowire was along the [011] direction. The mixed nanowires were randomly oriented and dispersed in PDMS without aggregations. Peak output voltage and current of the PyNG were 10 mV and 120 pA under a temperature change rate of 2 K s\(^{-1}\). Though PDMS decreases the volume efficiency of the PyNG, it realized the flexibility of the PyNG, which was important for practical applications.

Another candidate of the PyNG was nanofiber-based dabcoHReO\(_4\), which was reported by Isakov et al. (Figure 13)\(^{[108]}\). Uniform dabcoHReO\(_4\) fibers were fabricated by electrospinning process. The crystalline structure of dabcoHReO\(_4\) was examined by XRD, and the most intensive Bragg reflection was (200) followed by (110) in the fibers. Thus, the orientations of the dabcoHReO\(_4\) fibers were all aligned in one direction and had the same polarization. Raman spectroscopy also confirmed a single crystal orientation of dabcoHReO\(_4\) fibers. Piezoresponse force microscopy (PFM) was used to achieve hysteresis loop of piezoresponse and the piezoelectric coefficient was 20 pm V\(^{-1}\). Peak current output performance of the PyNG was 200 pA at temperature change rate of 0.2 K s\(^{-1}\). To evaluate the pyroelectric coefficient, the PyNG was constant heating and cooling, and the corresponding pyroelectric coefficient was 8.5 \(\mu\)C m\(^{-2}\) K\(^{-1}\).

Although fiber mat dabcoHReO\(_4\) had low pyroelectric constant than bulk dabcoHReO\(_4\), it was easier to incorporate into wearable electronic applications.
The other candidate of the PyNG was BTO ferroelectric material demonstrated by Ji et al. (Figure 14). A BTO ceramic disk was fabricated by dry press process for piezoelectric, pyroelectric and photoelectric material. BTO was covered by PDMS as a protective layer and a FEP film was attached on the PDMS as a triboelectric material; a nylon film attached on acrylic was used as counter triboelectric material; commercial thermoelectric module was used for thermal energy harvester. XRD patterns of the BTO confirmed tetragonal phase of BTO which was having ferroelectric property. The PyNG peak output voltage and current were 1.5 V and 15 nA, and the solar cell generated peak current and voltage of 40.5 nA and 0.8 V, and average current and voltage of 10 nA and 0.6 V, respectively. Output current of the TENG and PENG hybrid NG was 3.5 µA, but voltage was not distinctly detected (<0.1 V). The calculated pyroelectric coefficient of the hybrid NG was 26 nC cm\(^{-2}\) K\(^{-1}\). The coupling effect between PyNG and solar cell was evaluated by simultaneous heating/cooling and light irradiation. The enhancement ratio of the output current was 86% by coupling effect. They successfully demonstrated charging a 0.33 µF capacitor up to 1.1 V in 10 s using the coupled NG.

Qi et al. reported a photovoltaic-pyroelectric coupling effect based self-powered photodetector using BFO ferroelectric material (Figure 15). BFO powders were synthesis by hydrothermal method, and XRD measurement confirmed perovskite phase of the BFO. The Schottky barrier was formed at the interface of ITO/BFO and BFO/Ag. When the temperature change rate was 0.2 K s\(^{-1}\) under 450 nm light illumination condition, the ITO/BFO/Ag hybrid NG generated 0.13 V and 8.8 nA, but the photovoltaic current was 2 nA. Due to the differing optimum load resistances of the PyNG and solar cell, the hybrid NG had two optimum load resistances, which were the same as the optimum load resistance of PyNG and solar cell. The responsibility of the hybrid NG was 978% larger than normal solar cell, and the recovery time of the hybrid NG was 0.8 s after 450 nm light irradiation. They successfully demonstrated 3 × 3 photodetectors array for real-time signals mapping on a BFO disk with high resolution. Therefore, lead-free pyroelectric materials are also able to be used in various applications instead of PZT.

5. Other Application of the PyNG

Further development of the PyNGs requires innovative approach to practical applications and enhancement of pyroelectric coefficient. For example, the coupling effect between thermal nanophotonic and pyroelectric (TNPh-pyro) is one of the innovative candidates. Wang et al. utilized thermal nanophotonic effect to enhance pyroelectric output performance and to reflect useless solar irradiation retaining high transparency (Figure 16). Typically, PyNGs had limited thermal fluctuation, but TNPh-pyro effect was able to deviate the problem by deliberate channelling of the reflected NIR heat onto PVDF. The TNPh structure consisted of periodically layered TiO\(_2\) and mesoporous silicon dioxide (SiO\(_2\)) films, and topmost layer of mesoporous TiO\(_2\)/Cu. PVDF film was an outdoor solar
heat harvester and the TNPh layer reflected NIR irradiation, absorbed UV and transmitted visible light for cooling, air purification and lighting.\textsuperscript{[114]} The crystal structures of TiO\textsubscript{2} and SiO\textsubscript{2} were confirmed by XRD characterization and the NIR reflection characteristic of TNPh-pyro device showed that the NIR transmittance was 35\% and that the visible light transmittance was 69.5\%, which satisfied the typical transparency requirements of a window. Compare with bare glass and the TNPh-pyro device under 100 mW cm\textsuperscript{−2} solar irradiation, bare glass heated up to 33.1 °C and the TNPh-pyro device heated up to 29 °C, which was able to save up to 45\% of energy for the building's cooling.\textsuperscript{[115]} In addition, UV irradiation on TiO\textsubscript{2}/Cu film decreased ethanol, IPA and formaldehyde, and the TNPh-pyro device generated peak voltage and current of 8.2 V and 23.5 nA, respectively, that was 50\% enhanced output performance than pristine PVDF film. They successfully demonstrated that a TNPh-pyro-roofed house had 4.2 °C lower internal temperature than glass-roofed house with harvesting peak voltage and current of 32 V and 126 nA, respectively. Another requirement of the improving PyNGs is innovation of pyroelectric material. Although rapid temperate change rate control is able to increase output performance, the most important factor is pyroelectric
coefficient, which is unique property of material. Until now, the PyNGs have shown wide discrepancies in theoretical and experimental output performances due to imperfect material structure and property. Thus, heat transfer, internal polarization change, defects, working temperature condition and other physical parameters are necessarily improved.

6. Conclusion

The recent research results of emerging pyroelectric and hybrid nanogenerators are described in this paper. Polymer-based PyNGs are flexible, stretchable and biocompatible, so it is more suitable to use as wearable applications. Ceramic-based PyNGs have higher pyroelectric coefficient, thus its output power performance is much better than polymer-based PyNGs and more suitable for self-powered IoT systems. Table 1 shows a summary of materials, pyroelectric coefficient, working condition, output performance, efficiency and flexibility/stretchability of various PyNGs. In order to increase flexibility of PyNGs, micropatterned structure, nanowire structure, and fiber structure are effective approaches. Pyroelectric ceramic nanoparticle/nanowire embedded in flexible polymer is also able to have high flexibility. With the future development of pyroelectric materials, PyNGs may become important new energy harvesting technologies, but there remain the following challenges: Devices should ensure long cycle thermal and sun irradiation stability. If substrate or electrode cannot maintain the mechanical property by thermal and sun light induced damage, the life of system will be limited even

Figure 16. Schematic fabrication process of the thermal nanophotonic and pyroelectric coupled TNPh and practical application of TNPh-pyro device. Reproduced with permission.[111] Copyright 2017, American Chemical Society.
pyroelectric material can endure the thermal and sun irradiation induced damage. In addition, extremely high humidity in the atmosphere can react with pyroelectric materials and degrade its performance. Furthermore, spontaneous polarization of pyroelectric materials is depleted at higher temperature condition than Curie temperature. Specialized power management system is necessarily required for high efficient system. Nanoscale power consumed energy management system will significantly increase the energy conversion efficiency. Finally, pyroelectric material innovation, device structure optimization, and device packaging are crucial for high power energy harvesters. A systematic analysis of challenges can be solved by experimental and theoretical approaches, and multidisciplinary development from material science, electronics, and physics will advance output performance of PyNGs in the near future.

The advanced PyNGs will be able to endure practical environmental conditions and actualize new type of IoT power sources and self-powered sensors.

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Conflict of Interest
The authors declare no conflict of interest.

Table 1. A summary of materials, pyroelectric coefficient, working condition, output performance, efficiency, and flexibility/stretchability of various PyNGs.

<table>
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<td>[47]</td>
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<td>&gt;5 K, –</td>
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<td>18.5 K, 100 K s⁻¹</td>
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<td>–</td>
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<td>–</td>
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<td>ZnO</td>
<td>1.2–1.5</td>
<td>30 K, 1.8 K s⁻¹</td>
<td>18 mV, 0.4 nA</td>
<td>0.05–0.08 Vm² W⁻¹</td>
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<td>[99]</td>
<td>ZnO</td>
<td>–</td>
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<td>–, 2 µA</td>
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<td>22 V, 171 nA cm⁻²</td>
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<td>KNbO₃</td>
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<td>–</td>
<td>Yes</td>
<td>–</td>
</tr>
<tr>
<td>[108]</td>
<td>dabcOHReO₄</td>
<td>0.85</td>
<td>6 K, 0.2 K s⁻¹</td>
<td>–, 200 pA</td>
<td>14.8%</td>
<td>Yes</td>
<td>–</td>
</tr>
<tr>
<td>[109]</td>
<td>BTO</td>
<td>22.5–25.9</td>
<td>12 K, 0.85 K s⁻¹</td>
<td>6 V, 80 nA</td>
<td>–</td>
<td>Yes</td>
<td>–</td>
</tr>
<tr>
<td>[110]</td>
<td>BiFeO₃</td>
<td>–</td>
<td>1.86 K, 0.21 K s⁻¹</td>
<td>–, 5.5 nA</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[111]</td>
<td>PVDF</td>
<td>2.7</td>
<td>19 K, 1.7 K s⁻¹</td>
<td>8 V, 22 nA</td>
<td>–</td>
<td>Yes</td>
<td>–</td>
</tr>
</tbody>
</table>


