Topical Review

Nanostructured polymer-based piezoelectric and triboelectric materials and devices for energy harvesting applications

Qingshen Jing and Sohini Kar-Narayan

Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom

E-mail: sk568@cam.ac.uk

Received 19 June 2017, revised 26 April 2018
Accepted for publication 26 May 2018
Published 27 June 2018

Abstract
Harvesting energy from ambient mechanical sources in our environment has attracted considerable interest due to its potential to power applications such as ubiquitous wireless sensors and Internet of Things devices. In this context, piezoelectric and/or triboelectric materials offer a relatively simple means of directly converting mechanical energy from ubiquitous ambient vibrating sources into electrical power for microscale/nanoscale device applications. In particular, nanoscale energy harvesters, or nanogenerators, are capable of converting low-level ambient vibrations into electrical energy, thus are vital to the realization of the next generation of self-powered devices. Polymer-based nanogenerators are attractive as they are inherently flexible and robust, making them less prone to mechanical failure which is a key requirement for vibrational energy harvesters. They are also lightweight, easy and cheap to fabricate, lead-free and biocompatible, but in many cases their energy harvesting performance is found lacking in comparison to more commonly studied inorganic materials. Recent advances have been made in developing scalable nanofabrication techniques for flexible and low-cost polymer-based nanogenerators with improved energy conversion efficiency, including the incorporation of high-quality polymer nanowires with enhanced crystallinity, piezoelectric and/or surface charge properties. In this review, we discuss aspects of nanomaterials growth and energy harvester device design, including those involving nanowires of polymers of polyvinylidene fluoride and its co-polymers, nylon-11, and poly-lactic acid for scalable piezoelectric and triboelectric nanogenerator applications, as well as the design and performance of polymer-ceramic nanocomposite nanogenerators. In particular, we highlight the effects of growth parameters, nanoconfinement, self-poling, surface polarization, crystalline phases, and device assembly on the energy harvesting performance of a range of recently reported nanostructured polymer-based materials and devices.

Keywords: nanogenerator, piezoelectric, triboelectric, energy harvesting, ferroelectric polymer

(Some figures may appear in colour only in the online journal)
Introduction

Ambient sources of mechanical energy such as body movement, fluid/wind flow and machine vibrations, have great potential to be exploited in order to power wearable, embedded, implanted and/or portable electronics and sensors [1, 2]. In this review, we focus on two distinct types of vibrational energy harvesters, namely piezoelectric and triboelectric energy harvesters, that can directly convert ambient mechanical energy into electricity. In particular, we consider recent developments whereby nanomaterials with enhanced relevant physical properties have been incorporated into so-called nanogenerators (NGs) for low-power applications. In the case of piezoelectric NGs, inorganic ceramic piezoelectric materials such as lead zirconium titanate (PZT) and zinc oxide have been well-studied due to their high piezoelectric coefficients ($d_n$). Ceramic-based NGs, however, suffer from being rigid and fragile, and in general unsuitable for continuous application, particularly under prolonged and/or extreme mechanical conditions. On the other hand, piezoelectric polymers, some of which are ferroelectric and show significant piezoelectric properties particularly at the nanoscale [1, 3], such as polyvinylidene fluoride (PVDF) and its copolymers, as well as certain polyamides (nylons) in the appropriate crystalline phases, are prime candidates for piezoelectric NGs that are flexible, robust, light, cheap, as well as biocompatible.

Ferroelectric polymers happen to be very well-suited for triboelectric energy harvesting applications as well [4]. Triboelectric energy harvesters can be realized by combining pairs of dissimilar materials whereby charge is transferred between the surfaces due to contact and separation through relative mechanical motion [5, 6]. The performance of a triboelectric energy harvester is largely governed by pairing materials chosen according to an empirical ‘triboelectric series’ which lists materials by their electron-donating (tribo-positive) or electron-accepting (tribo-negative) tendencies. Pairing materials at opposite ends of the triboelectric series leads to better charge generation and extraction through triboelectric energy harvesting schemes. PVDF and nylon, for example, are situated at extreme positions in this series and are therefore suitable for incorporation into triboelectric energy harvesters. Importantly, due to their surface polarisation properties and feasibility of surface modification especially at the nanoscale, it is possible to tune and improve the performance of triboelectric energy harvesters by controllably tuning the surface charge properties of the constituent ferroelectric polymers. Given that there exist common polymeric nanomaterials for applications in both piezoelectric and triboelectric energy harvesters, this review covers the two polymer-based approaches, including the materials and device challenges therein. The focus will be on their fabrication and incorporation into energy harvesting devices, with insight into how progress can be achieved in this field through a nano-engineering based approach.

1. Piezoelectric polymers

The piezoelectric effect is an electromechanical coupling effect resulting in the interconversion of mechanical and electrical energy, which in some cases manifests more strongly in nanoscale systems than in the bulk. Based on this phenomenon, piezoelectric NGs were first demonstrated using ZnO nanowires (NWs) [7–9]. Since then, many nanogenerator studies have focused on rigid piezoelectric ceramic materials such as PZT [10], ZnO [9, 11], GaN [12], NaNbO3 [13], etc. However, NGs in operation are required to sustain continuous and periodic mechanical deformations, such as pressing, stretching or bending, which is often incompatible with the brittle nature of inorganic or ceramic piezoelectrics, giving rise to mechanical failure and/or degradation of NG performance over time. Piezoelectric polymers, such as PVDF and its copolymers, have been found to possess good piezoelectric properties [14, 15], while being flexible and mechanically robust. PVDF [(CH2–CF2)n] consists of a carbon backbone with each carbon in the chain alternatively binding two fluorine or two hydrogen atoms, oriented on opposite sides of the carbon chain, as shown in figure 1. The piezoelectric properties of PVDF arise from the large difference in electronegativity between the fluorine and carbon atoms compared with the hydrogen atoms. This results in polar bonds and a resulting dipole moment from the fluorine side of the chain towards the hydrogen side [16]. Within the larger polymer structure the dipole moments may sum to give a net electric dipole moment depending on the crystalline geometry (figure 1(a)). NGs made from PVDF films present good robustness, reliability and flexibility [17, 18]. However, the ability to control the required piezoelectric crystalline phase in confined geometries [19, 20] has received considerable attention in recent times. In general, typical thin film fabrication often results in α phase PVDF (shown in figure 1(a)) which does not behave exhibit piezoelectricity due to net cancellation of dipoles along the chain [16]. Poling with either mechanical stretching, electric field or from controlled growth may force the polymer into a ferroelectric polar β phase which exhibits the strongest piezoelectricity [20–24]. Co-polymers of PVDF where some of the hydrogen atoms are replaced with fluorine atoms are more likely to crystallise in a polar phase due to steric factors. Even then, it has been reported that electrically poled P(VDF-TrFE) nanowire arrays could have over 10 times higher piezoelectric coefficients than normal P(VDF-TrFE) thin films undergoing the same treatment [25]. More recently, nanowire synthesis approaches making use of a nanoconfinement growth effect have been found to be more likely to result in so-called ‘self-poled’ β phase NWs [21, 26], mostly observed, for example, in template-assisted growth whereby polymer NWs are grown within nanoporous templates by infiltration from solution or melt, and where the resulting NWs do not require external electrical poling in order to exhibit piezoelectric behaviour. Self-poling results from some degree of molecular alignment of the polymer chains along the length of the nanowire, which may arise as a result of the high degree of shear force experienced by the polymer solution during capillary infiltration. Typically the infiltration is carried out at elevated temperatures, giving rise to high chain mobility that enables the polymer to crystallise in this aligned state. Figure 1(b) shows an example of crystallization of template-grown PVDF NWs characterized by x-ray diffraction (XRD) studies, where only
the polar $\beta$ phase is identified, as opposed to a mix of crystallographic phases observed in thin films of the same material.

Polyamides, commonly known as nylons, are another group of polymers that have potential NG applications. Odd-numbered nylons, being named after the number of carbon atoms in a repeating unit of $[\text{HN}-(\text{CH}_2)_x-\text{CO}]_n$, contain pairs of $-\text{NH}$ and $-\text{C}=\text{O}$ amide groups in the same direction that form essential and stable dipole moments (figure 2(a)), which leads to their observed ferroelectric and piezoelectric behaviour [27, 28]. In comparison, these groups in even-numbered nylons are aligned in an alternating fashion leading to the net cancellation of dipoles along the chain (figure 2(a)). The crystalline structure of nylon-11 has been extensively studied due to its extensive degree of polymorphism. Nylon-11 displays several crystal structures depending on the processing conditions. In terms of electrical property, although all nylon-11 has a polar crystalline phase due to its molecular configuration, the electric polarisation can be maximised from a specific type of crystalline phase, for example, the highest electric polarisation has been observed from the meta-stable pseudo-hexagonal phases ($\gamma, \gamma', \delta'$) [27, 29, 30].

As in the case of PVDF, bulk or thin films of odd-numbered nylons usually contain a variety of phases that need to be mechanically or electrically poled to achieve the electroactive polar phase. However, template-assisted nanoconfined growth processes have been shown to be very effective in controlling the required piezoelectric crystalline phase and its alignment to give rise to self-poled piezoelectric polymer NWs [31], without the requirement of external poling procedures. Figure 2(b) shows an example of different crystalline phases observed by XRD in nylon-11 NWs grown within porous AAO templates, where the required pseudo-hexagonal phase was successfully realised as a result of the nanoconfined template-assisted growth process [31].

Apart from PVDF and nylon, piezoelectric properties have been reported in other polymers including, polylactic acid (poly-L-lactic acid with shear piezoelectricity, in particular) [32, 33] (figures 3(a) and (b)), polyurea [34, 35] and cellulose.
In the case of poly-L-lactic acid (PLLA), there are four known crystal phases (α', α, β and γ) based around a helical conformation of the polymer chain. It is not well understood which of these crystal phases is required for piezoelectricity, if indeed any in particular [38]. Given the similarities between the crystal structures, it seems unlikely that only one specific crystal phase is responsible for the piezoelectric properties. This is quite unlike other piezoelectric polymers, such as PVDF, where the polar β phase is necessary for piezoelectricity. As in the case of PVDF and nylon-11, template-assisted growth of PLLA NWs was found to result in highly aligned and crystalline NWs, where the crystallinity could be precisely controlled via the infiltration temperature during the template wetting growth process [38]. Figure 3(b) shows XRD patterns of as-grown PLLA NWs within the template where only one significant reflection attributed to inter-chain scattering from (1 1 0) & (2 0 0) planes was observed, and PLLA NWs freed from the template where many more reflections were observed producing a pattern consistent with the α phase.

In this review, we will particularly focus on polymeric NWs that show certain types of ferroelectric or piezoelectric behaviours resulting from their fabrication process and crystalline properties, and their subsequent performance as energy harvesters.

2. Triboelectric polymers

Triboelectric charges are generated when surfaces of two materials with different surface potentials are brought into contact, with electrons injected at the interface from one material to another [6, 39, 40]. The flow direction of the electrons can be predicted by an empirically determined series called triboelectric series [40, 41], where materials at the tribo-negative end of the series are likely to accept electrons while those at the tribo-positive end are likely to donate electrons. Depending on the dielectric property of the materials, charges may remain on the surfaces when separated, thus uncompensated dipoles are generated. Triboelectric energy harvesters have been developed that take advantage of this contact electrification phenomenon which can then be harnessed to convert periodic mechanical motion into electricity via electrostatic induction [5]. Polymers have featured prominently in triboelectric energy harvesters not only because several candidates in the triboelectric series are polymeric, but also due to their mechanical robustness, dielectric properties and ease of fabrication.

Researchers have tried to improve the performance of triboelectric energy harvesters through different strategies, most common of which are surface roughness modification and surface charge distribution tuning [6]. To increase roughness, nanopatterns, nanostructures, nanoparticles or NWs are incorporated into the surface to increase the contact surface area [42–47]. On the other hand, to tune the surface charge density, charges could be directly injected onto the contact surface [48]. Another strategy involves embedding electrically poled ferroelectric nanoparticles in the triboelectric material [49, 50], showing highly enhanced outputs as compared to untreated films. Such modifications have been mostly conducted on or in tribo-negative polymers, such as PVDF, polytetrafluoroethylene (PTFE, or teflon), polyurethane (PU), with far less focus on polymers from the tribo-positive side of the series. Although tribo-positive polymeric candidates are limited, nylon, particularly in the form of odd-numbered ferroelectric nylon NWs, is a notable exception that has been reported to result in enhanced triboelectric energy harvesting performance [51], as will be reviewed in the following sections.

3. Growth of polymer-based NWs for energy harvesting applications

Since polymers are in general shape-adaptable, there have been many reports on the growth of various polymer NWs using both top-down or bottom-up approaches. In particular, for NG applications, these nanostructures are often required to possess ferroelectric or piezoelectric properties which requires the polymeric material to be either single crystalline, which is generally unfeasible, or to be polycrystalline with polarization in the individual lamellae aligned along the same direction, i.e. the material should be ‘poled’. Often the poling process is conducted on the NWs post-synthesis by applying strain or large electric field, however, this might bring unnecessary structural deformation or require extra post-processing
steps that add to the complexity of the growth process. Thus, one-step nanofabrication processes that enable self-poling in the as-grown NWs are highly sought after due to the ease and convenience of synthesis.

3.1. Top-down approaches

Top-down approaches usually take advantage of etching processes to achieve the desired polymeric nanostructures. Fang et al reported a polymer nanowire fabrication method by ion etching polymer films covered with metal nanoparticles as masks, which can be adopted to a large variety of polymeric materials [52]. Au, Pt, Ti, Al or metals of similar nature were first sputtered on top of the polymer films of interest, forming a thin layer to act as a nanoscale mask. Inductively coupled plasma was then applied on top to create the surface roughness of the polymer, leaving pillar like polymer NWs standing on the substrate of choice (figures 4(a) and (b)). The density and length of the NWs could be controlled by controlling the thickness of the sputtered metal layer and the plasma etching time. The method is easily adaptable and thus it is possible to make polymer nanowire arrays with strong piezoelectric or ferroelectric properties from already poled polymer films. Another top-down method reported involved a nanoimprinting process [25]. In this method, a silicon mould with nanopillar structure was made by hydrogen plasma etching and covering with the anti-stick coating. P(VDF-TrFE) thin films were then thermally nanoimprinted from the mould to form grass-like nanopillar arrays, as shown in figures 4(c) and (d).

3.2. Bottom-up approaches

3.2.1. Electrospun NWs. Electrospinning has been a widely adopted nanowire synthesis method for a large selection of polymers. The polymer solution from which the NWs are fabricated is first fed through a nozzle using a mechanical pump or syringe (see figure 5). A large voltage source, in the region of 5–50 kV, is applied to create a large electric field in the solution which results in its accumulation at the tip of the nozzle. Competing dynamics associated with the induced electrostatic repulsive force in the solution and its surface tension result in the formation of a droplet which is known as a Taylor cone. As the repulsive force overcomes the surface tension, a jet of material is extruded from the Taylor cone. The jet begins to dry in flight as it becomes further elongated due to the electrostatic repulsion which also results in the jet moving with a ‘whirling’ spinning motion before subsequently being collected on a grounded surface [53, 54]. In general, electrospinning does not trivially allow for aligned NWs with uniform size distribution, but does require large voltages for
nanowire fabrication. Electrospun NWs can be relatively long due to the continuous ejection process with diameters of order 100–1000 nm [55–57]. What makes this method preferable for piezoelectric and ferroelectric polymer nanowire fabrication is that the voltage applied for electrospinning also serves to polarize the polymer at the same time [58, 59], and it may be possible to control the alignment with proper movement of the collecting plate/roller (figure 5).

3.2.2. Template-assisted polymer nanowire growth. Compared with etching or electrospinning which either requires specific equipment or extreme conditions like high voltage, template-assisted nanowire growth can be a relatively mild and simple synthesis approach. In this method, a polymer melt or solution is infiltrated into a nanoporous template. Subsequent solidification from the melt, or evaporation of the solvent of the solution, results in polymer nanostructures defined by the geometry of the template [60, 61]. A good selection of templates including anodic aluminum oxide (AAO), polycarbonate (PC), polyimide (PI), etc, can be easily fabricated and are even commercially available. Due to the confinement effect during the growth process, polymer NWs with ferroelectric or piezoelectric properties have been found to grow in an aligned manner inside the nanopores [26, 62], showing consistent poling direction along the nanowire axis, and resulting in high piezoelectric coefficients [19, 20]. Removal of the template depends largely on the type of the template and the property of the polymer NWs, with common approaches including burning away the template [63] or chemical etching with solvent [38]. As for NG fabrication, sometimes the template removal process might be unnecessary as the template could serve to keep the NWs aligned with added mechanical advantages such as robustness and flexibility, and shielding from environmental degradation [63, 64].

A series of methods on the template-assisted growth of NWs, eventually aimed at fabrication of NGs are listed in figure 6. There are different ways of achieving polymer-based NGs, including some in which the host template is polymeric while the NWs grown are inorganic. Figure 6(a) shows polymer solution [1, 24] or melted polymer [65] being infiltrated into the template, with the template being wetted by the polymer filling into the nanopores. Figure 6(b) illustrates a template being placed floating above the heated polymer solution, where capillary force pulls the polymer up along the pores [31, 38]. Although NWs synthesised by these methods have been reported to show certain polarization preference [19, 20], the crystallization during infiltration, however, can be further adjusted by applying gas flow on top of the template to control the temperature distribution, namely, gas-flow assisted nano-template (GANT) nanowire growth method [51] (figure 6(c)). Some examples of polymer-ceramic nanocomposite NGs using polymeric templates are also included in figures 6(d) and (e), where the piezoelectric active material is ZnO NWs. In these examples, the piezoelectric ZnO NWs were grown either by hydrothermal synthesis [64] (figure 6(d)) or by electrodeposition [63] (figure 6(e)) within the nanopores of a polycarbonate template. All the template-assisted synthesis methods compared in this figure will be further discussed in detail in the following sections of the review.

4. Energy harvesters based on PVDF and its copolymers

4.1. Polymer-Ceramic nanocomposite NG with piezo-active polymers

PVDF and its co-polymers (e.g. P(VDF-TrFE)) exhibit good piezoelectric properties that are comparable to some ceramic piezoelectric materials [1, 3]. PVDF NWs are particularly attractive for mechanical energy harvesting due to their robust mechanical properties with excellent chemical stability. Difficulties of fabricating PVDF nanowire-based piezoelectric NGs mostly lie in two aspects, which include (i) finding scalable fabrication methods and (ii) poling the polymer for required piezoelectric performance. In the latter consideration, poling typically requires high electric fields (up to the order of 10^5 V m^{-1}) or mechanical stretching, both of which are not necessarily practical when dealing with NWs. Whiter et al reported a template-assisted approach for scalable growth of self-poled (P(VDF-TrFE)) nanowire arrays and their application in NGs [21]. To start the synthesis process, AAO template was prepared with a thin layer (~15 nm) of silver deposited on one side of the surface, which was required for easy and complete removal of the residual film formed...
after the complete infiltration of the polymer. P(VDF-TrFE) solution was prepared by dissolving the polymer powder in butan-2-ol. The solution was then dropped and left on top of the Ag-coated AAO template at 60 °C for several hours for full infiltration. The P(VDF-TrFE) thin residual film formed was removed by chemical and plasma etching process, leaving only polymer NWs contained in the template (complete fabrication process is shown in figure 7(a)). To examine the crystallization of as-synthesized NWs, freed NWs (AAO template dissolved by aqueous phosphoric acid solution) were characterized by XRD with diffraction patterns reflecting only (2 0 0) and (1 1 0) planes of crystalline phase $\beta$, as compared with parent P(VDF-TrFE) powder samples showing peaks of all $\alpha$, $\beta$, $\gamma$ phases (figure 7(b)). The stronger $\beta$ phase character of the NWs was believed to be solely due to the confinement effect of the nanoporous template [19, 20, 26, 62, 66, 67], which was beneficial to their subsequent implementation into NGs. Template-grown P(VDF-TrFE) NWs still embedded within the template were then incorporated into an NG, by sputtering platinum electrodes on both sides of the nanowire-filled template, followed by encapsulation in poly(dimethylsiloxane) (PDMS) (figure 7(c)). The NG was then mounted onto a fixed surface against a magnet shaker with oscillating pressure being applied perpendicular to the surface (parallel to the axis of the NWs) of the NG, as shown in figure 7(c). Typical output performance of the NG in this testing system is shown in figures 7(d) and (e) at impact frequency of 5 Hz and vibration amplitude of 1 mm. Peak output voltage of 3 V and current of 5.5 nA was observed and the energy conversion efficiency of the template-grown P(VDF-TrFE) NWs was found to be around 11%, while the overall device efficiency was found to be 0.2%. The latter can be significantly improved by switching to a softer template, such as polyimide [24] which requires less mechanical energy for axial deformation than AAO. The energy harvesting ability of the NG was further demonstrated by charging capacitors following rectification of the NG ac electrical output, which were then discharged to successfully light up an LED. Importantly, the template-based P(VDF-TrFE) nanowire NG showed excellent fatigue performance over $\sim 10^6$ continuous impacting cycles.

A template-wetting approach for P(VDF-TrFE) nanotube synthesis was also reported by Bhavanasi et al where the nanotubes were found to predominantly crystallise in the $\beta$ phase, with preferred polarization direction along the long axis of the nanotubes [65]. The synthesis started with fabricating a thin film (30 µm) of P(VDF-TrFE) by drop casting, followed by annealing at 135 °C. The film was then placed on top of a commercial AAO nanoporous template and heated up to 175 °C which was above the melting point of P(VDF-TrFE), at which temperature the polymer wetted the template. The P(VDF-TrFE) in the template was then annealed again at 135 °C, with the top residual layer removed by polishing and etching if required. XRD patterns comparing embedded P(VDF-TrFE) nanotubes with films is showed in figure 8(a). Peaks of 19.8° corresponding to planes (2 0 0) or (1 1 0) from both nanotubes and films indicate the piezoelectric $\beta$ phase, while the peak corresponding to the $c$-axis orientation at 201° or

| Description | Example template | Example Grown NW |
|-------------|------------------|-----------------|
| a)          | Material solution dropped on top of the template | AAO/PI | P(VDF-TrFE)[1][24] |
| b)          | Template placed above solution | AAO | PLLA [38], Nylon [31] |
| c)          | Gas-assisted template confined growth | AAO | Nylon-11 [51] |
| d)          | Template-assisted thermohydral growth | PC | ZnO [64] |
| e)          | Template-assisted electrodeposition growth | PC | ZnO [63] |

Figure 6. A list of template-assisted nanowire growth methods particularly aimed for energy harvesting. (a)–(e) Schematic illustrations of various growth methods with descriptions of the methods, template types, and materials grown.
(101) showed up in the film but was negligible in the nanotube samples. In this work, the authors fabricated an NG with the nanotubes freed from the template. In order to achieve this, the template was dissolved in NaOH, leaving freed nanotubes still attached onto the residual layer of (PVDF-TrFE) at the bottom. A thin layer of poly(methyl methacrylate) (PMMA) was formed on top of the nanotubes as insulator followed with gold deposited on both top and bottom as the electrodes (figure 8(b)). The NG was tested with a series of impacting pressures at 1 Hz from 0.008 MPa to 0.075 MPa, producing a peak output voltage from 0.3 V to 4.8 V. Maximum power density from this NG was achieved at 2.2 μW cm⁻² at external load around 600 kΩ. In comparison, an energy harvester made from a poled PVDF-TrFE thin film operated at the same condition produced a maximum voltage and power density of 0.8 V and 0.06 μW cm⁻², respectively (figures 8(c) and (d)).

4.2. Electrospun P(VDF-TrFE) nanofiber hybrid NGs
Spin-coated PVDF thin films have previously been adopted in piezoelectric NG fabrication [68]. To acquire further improvement, Wang et al proposed an electrospun P(VDF-TrFE)
nanofiber based piezoelectric NG as part of their hybrid NG, which also includes a PDMS/MWCNT (multi-wall carbon nanotube) triboelectric nanogenerator [69]. The NG contained two parts with respective fabrication processes shown in figure 9(a). Polymer solution was prepared from dissolving P(VDF-TrFE) in N–N dimethylformamide (DMF) and acetone. A voltage of 10 kV over a distance of 10 cm between syringe tip and collector was applied in the electrospinning process, generating P(VDF-TrFE) nanofibers with diameter around 200 nm (figure 9(b)) which were collected on a metal electrode. Due to the polarization effect from the high electrospinning voltage, dominant \( \beta \) crystalline phase required for piezoelectric NG operation was formed within the nanofibers as proven by XRD (figure 9(c)). The top surface of the nanofibers was covered by another layer of screen-printed electrode, to form a packaged piezoelectric NG. The second part comprising micro-patterned MWCNT-doped PDMS friction layer was fabricated using photolithographic Si mould to form the triboelectric part of the hybrid NG. The individual output open circuit voltage of the triboelectric and piezoelectric parts could reach up to 13 V and 1.3 V, respectively, with combined rectified voltage accumulated up to 17 V (figures 9(d) and (e)) under the adopted testing conditions in the work. To demonstrate the energy harvesting performance enhancement effect arising from P(VDF-TrFE) nanofibers and doping of MWCNT, spin coated P(VDF-TrFE) films and untreated PDMS were fabricated into NGs for control purposes, showing an improved output from the former combinations.

5. Energy harvesters based on nylon

5.1. Nylon nanowire-based piezoelectric NG

There have been relatively few reports of polymers other than PVDF and its co-polymers that have ferroelectric or piezoelectric properties, and which have been reported as an active material in piezoelectric NG fabrication. However, the typically low Curie and/or melting temperatures of PVDF and its co-polymers limit their applications at higher temperatures, compared with their piezoelectric ceramics counterparts. Therefore, there is a need for developing thermally stable piezoelectric polymers for energy harvesting over a wider temperature range above room temperature. Driven by this motivation, Datta et al adopted odd-numbered nylons as candidates for piezoelectric NGs [31]. Odd-numbered nylons, such as nylon-11, are known to have ferroelectric and piezoelectric properties due to the high degree of hydrogen bonding and dipole orientation resulting from the arrangement of polyamide molecules within adjacent chains upon crystallization [70]. Meanwhile, nylons have relatively high melting temperature compared with PVDF and at the same time their excellent mechanical properties have been well-known in textile industry for fabrics [71].

Among odd-numbered nylons, nylon-11 possesses ferroelectric and piezoelectric properties that are comparable with those of PVDF [72–75], with a reported piezoelectric charge constant \( d_{31} \) ranging from 3 to 15 pC/N, through different
approaches including strained, melting-quenched, solution-cast and poled thin-films, at various temperatures [27, 28, 76, 77]. Datta et al. described a facile and scalable synthesis approach to fabricate piezoelectric nylon-11 nanowire arrays with a uniform size based on AAO template-assisted solution-processed capillary infiltration. The synthesis mechanism and fabrication process are schematically shown in figure 10(a). The process comprised of three steps, which include (i) preparation of 10 wt% nylon-11 solution in formic acid, from nylon-11 pellets, (ii) growth of nylon-11 NWs relying on the capillary action when placing an AAO template on the nylon-11 solution pool, and (iii) cleaning of any excess nylon-11 nanoparticles adhered to the top of the AAO template due to the capillary wetting process and subsequent formic acid solvent evaporation. The as-grown NWs in the template could be further transferred to any substrate by dissolving the AAO in phosphoric acid. In this work, the morphology of the NWs was largely determined by the concentration of the nylon solution, with an optimum 10 wt% concentration resulting in the highest nanowire aspect ratio, with lengths of 40–50 µm and nanowire diameters of ~200 nm (figure 10(b)). Further tests from XRD, room-temperature Fourier transform infrared spectroscopy and differential scanning calorimetry measurements showed that the NWs were composed with both α and γ phases nylon-11, the latter of which is particularly relevant for piezoelectric applications.

A piezoelectric NG based on the template-grown vertically aligned nylon-11 NWs was then fabricated by depositing gold electrodes on both sides of the filled template (figure 10(c)). The NG was tested over different impacting frequencies from 5 Hz to 20 Hz at forces akin to finger tapping with peak open circuit output up to 1 V and peak short circuit output up to 100 nA, which is comparable with those generated from P(VDF-TrFE) piezoelectric NGs made from similar approaches and under similar mechanical excitation [21]. What is noteworthy is that the nylon-11 based piezoelectric NG was capable of operating at a relatively high temperature up to 150 °C in a reliable manner (figure 10(d)), with the performance at room temperature being recovered upon cooling. Fatigue testing was also carried out to show good reliable performance over prolonged continuous testing (~270000 cycles). This makes it possible to use such a polymer-based

Figure 9. Hybrid NG with a electrospun P(VDF-TrFE) nanofibers based piezoelectric NG and PDMS/MWCNT based triboelectric NG. (a) Schematic structure of the hybrid NG. (b) Electrospun P(VDF-TrFE) nanofibers. (c) XRD for as-synthesized nanofibers. (d) Electric connection and rectifying circuit for hybrid NG. (e) Rectified voltage output. Reproduced from [69]. CC BY 4.0.
piezoelectric NG to harvest mechanical energy from high-temperature environments such as working car engines or heavy machinery.

5.2. Nylon nanowire-based triboelectric NG

A large proportion of tribo-positive materials [4, 40] include biological or natural materials, such as human skin and cotton, which have poor mechanical stiffness or lack of shape controllability [78]. Polyamides, or nylons, are notable exceptions as electron-donating polymeric materials, that are highly tribo-positive and whose shape and morphology can be controlled during initial synthesis or post-deposition. Nylon has been proved to perform better as the tribo-positive counterpart of triboelectric energy harvesters, as compared with aluminum or copper which are also commonly chosen [79, 80] due to ease of fabrication, but which are less tribo-positive than nylon.

Odd-numbered nylons have proven to be particularly attractive for application in triboelectric energy harvesters due to their ferroelectric properties. In this section, we review a recent work by Choi et al where self-polled nylon-11 NWs have been employed in triboelectric NGs [51]. The enhancement of surface charge density resulting from the polarization of the nylon-11 NWs led to a dramatically improved triboelectric energy harvesting performance. It has been previously reported that polarized ferroelectric polymers in triboelectric NGs could enhance the power output [49], due to an increased surface charge density due to the remnant polarisation of the material. However, the dipolar alignment of these polymers in the appropriate crystalline phase usually requires extreme conditions such as melt-quenching, undertaking mechanical stretching or applying large electric fields. In order to circumvent these issues, an innovative GANT infiltration method was put forward for the fabrication of ‘self-polled’ δ'-phase nylon-11 NWs. Compared with the previously discussed template-growth method in figure 10(a), the gas-flow assisted template-induced method in figure 11(a) requires the additional presence of an assisted gas flow on top of the template during the template-wetting process, which is the key factor giving rise to the production of polarized δ'-phase nylon-11 NWs (figure 11(b)). 17.5 w% nylon-11 in formic acid at 70 °C was used as pool solution with AAO template placed on top. Assisted gas flow rates from 0 m s⁻¹ to 3 m s⁻¹ were studied with 3 m s⁻¹ giving the best intensity of δ'-phase nylon-11 NWs at a dominant 2θ = 21.6° peak from XRD analysis (figure 11(c)). Compared with conventional melt-quenching methods for making δ'-phase nylon-11, the GANT method produced a larger amount of crystalline region within the NWs per unit area, as seen by XRD. The phenomenon was explained to be a temperature determined cooling effect from their simulation shown in figures 11(d) and (e).

Figure 10. Template assisted nylon-11 NWs based piezoelectric NG. (a) Schematics for nylon nanowire synthesis. (b) Nanowire length related to nylon solution concentration. (c) Piezoelectric NG made from nylon NWs embedded AAO template. (d) Piezoelectric NG outputs showing thermal stability up to 150 °C. [31] John Wiley & Sons. © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
force microscopy (KPFM) (figure 11(f)). A higher average surface potential of 426 mV was obtained from nanowire-filled templates in contrast with 82 mV from melt-quenched films, which was due to the ‘upward’ direction of the self-poled NWs. A triboelectric NG was fabricated using self-poled δ'-phase nylon-11 NWs embedded within AAO template, with the other side of the template coated by Au electrode, and with an Au-coated teflon substrate as the tribo-negative counterpart. The performance of the as-fabricated triboelectric NG, including open circuit voltage, short circuit current and output power density is shown in figures 11(g) and (h), with the performance compared to a teflon/Al triboelectric NG and a teflon/nylon film triboelectric NG. Due to the enhancement of the surface charge density as a result of having self-poled NWs, higher triboelectric potential and current was obtained from the self-poled nylon-11 nanowire-based triboelectric NG. Substantially higher power output (up to 10 times higher) was obtained from the nylon-11 nanowire-based triboelectric NG than from the other two triboelectric NGs. Due to the protective effect of the AAO nanopore template on the encapsulated nylon-11 NWs within, such an energy harvester showed little decay either in fatigue test (~540000 cycles) or in high humidity condition (~ 80%), with the latter known to promote nylon degradation in the absence of the protective template.

In contrast with the aligned nylon-11 nanowire-based triboelectric NG described above, a separate nanowire-based NG was fabricated in the same study using nylon-11 NWs that were freed from the template and which formed a randomly aligned nanowire mat lying on a substrate [51]. The triboelectric energy harvesting performance obtained from these randomly aligned NWs was substantially lower due to random orientation of polarization even though the mat had a smaller thickness and a rougher surface, which were believed to be the main beneficial factors for triboelectric NG output. Thus, conclusions were drawn that by using gas-assisted template method, δ'-phase nylon-11 NWs were successfully fabricated and adopted in triboelectric NG with significant improvement on output compared to regular nylon-based triboelectric NGs due to the enhanced surface charge arising from the self-poled aligned NWs.

6. Energy harvesters based on polylactic acid

6.1. Template-grown poly-L-lactic acid exhibiting with shear piezoelectricity

Among polymers that possess piezoelectric properties, poly-L-lactic acid (PLLA) is special due to its helical conformation
of the polymer chain leading to an inherent shear piezoelectricity [81–83] (figure 3), which is the coupling between a uniaxial polarisation and a shear stress or strain. PLLA is bio-compatible and bio-degradable [84–86], making it a potential functional material for in vivo energy harvesting or biomedical sensing. PLLA crystallised in four known phases ($\alpha'$, $\alpha$, $\beta$ and $\gamma$) all of which are based around the helical conformation of the polymer chain. Although a mechanism relating the crystal structure to the piezoelectric properties of PLLA has yet to be satisfactorily formulated, it is well known that both crystallinity and alignment of the polymer chains are required to reveal the shear piezoelectric behaviour. While piezoelectric NGs based on template-grown PLLA NWs have not been reported yet, attempts on fabricating and characterizing highly crystalline PLLA NWs via template-wetting with good shear piezoelectric properties have been conducted. Smith et al have reported the first direct observation of shear piezoelectricity in individual PLLA NWs [38], which were synthesized using a template-wetting method that allowed controllable and higher crystallinity compared with commonly used electrospinning method [87]. In the fabrication method shown in figures 12(a) (i)–(v), silver capped AAO template was placed floating onto heated solution of 10 wt.% PLLA in 1,4-dioxane. Capillary forces caused the solution to infiltrate into the porous template. Ag and solution residue were then removed followed with AAO template etching in phosphoric acid to release the PLLA NWs (figure 12(a)(vi)). It was found that by heating the PLLA solution to different temperatures during infiltration, the crystallinity of the nanowire could be reliably controlled (figure 12(b)). Temperatures above the glass transition temperature of PLLA (~60 °C) [85] enabled enhanced chain mobility which subsequently led to improved crystallisation during the nano-confined growth within the template pores. Crystallinity of up to 70% ± 5% was achieved with starting solution temperature at 100 °C, compared with typical 30%–40% from electrospun nanofibers [88–90], as verified by XRD data (figure 12(c)).

Piezo-response force microscopy (PFM) scanning data with 10 V oscillating potential over a laterally placed single PLLA nanowire [38] is shown in figures 12(d) and (e). Scans were only conducted at ~45° direction to the long axis of the nanowire to minimize possible nanowire movement caused by the tip. To prove the deflection distribution is actually a result of shear piezoelectricity, different oscillating scanning potentials were used and the data (figures 12(d) and (e)) was compared with finite element analysis (FEA) simulation models (figures 12(f) and (g)) to verify that the PLLA NWs did indeed exhibit shear piezoelectricity, and a piezoelectric tensor component $d_{14} \approx 8 \text{ pC/N}$ was estimated based.
on the analysis. Subsequently, a novel non-destructive PFM (ND-PFM) technique was developed and applied to the study of PLLA NWs. To minimize the influence from the tip on the sample, an intermittent contact mode was adopted by oscillating the tip for discontinuous contact on the sample and simultaneously applying an AC bias between the tip and the sample for piezoelectric response extraction at the points of contact [91]. These studies showed that the piezoelectric tensor could be directly evaluated from a combination of non-destructive scans on a single PLLA nanowire from both parallel and transverse orientations.

6.2. Electrospun poly-L-lactic acid nanofibers for strain sensing and energy harvesting

Although template-grown PLLA NWs have not been reported in piezoelectric NG applications, there are studies involving PLLA nanofibers grown by electrospinning which have been incorporated into self-powered strain sensors and energy harvesters [92]. Due to the requirement of high electric field in the electrospinning fabrication process, the resulting PLLA nanofibers were polarized along the nanofiber axis during the electrospinning process itself. The relatively long nanofibers generated from this method were found to be suitable for large-scale NG fabrication. In the work [92] reported by Zhu et al., a polyimide (PI) substrate with comb-shaped gold electrodes was first prepared and attached onto a rolling collector, rotating at 1800 rpm. PLLA solution (dichloromethane (DCM) as solvent) was sprayed onto the rolling substrate from a nozzle 10 cm away, under the application of a high voltage up to 15kV between the nozzle and substrate (figure 13(a)). The as-fabricated PLLA nanofibers had diameters in the range from 100 nm to 2 µm (figure 13(b)), showing a dominant α crystal phase with a left-handed (010) helicity confirmed by XRD. The observed spiral chain structure resulted in a piezoelectric potential being generated across the ends of the nanofibers upon bending, as proved from FEA simulations. As an energy harvester, electric charge was generated across the nanofibers and collected via the Au comb electrodes, with both open-circuit voltage and short-circuit current showing reasonable linearity as a function of deformation (figure 13(c)). Magnitudes of 200–500 mV in voltage and 100–200 pA current were generated using the mechanical setup described in the work [92]. A maximum power of 19.5 nW

Figure 13. (a) Electrospinning setup for PLLA nanowire fabrication. (b) SEM image of as-fabricated PLLA NWs. (c) Output signals of the electrospun PLLA NWs-based NG. [92] 2017 © Springer Science and Business Media New York 2017. With permission of Springer.
6.3. Electrospun polylactic acid for biodegradable triboelectric energy harvesters

Triboelectric energy harvesters do not require the constituent materials to be piezoelectric in order to function as such, even though the enhanced surface charge properties of such materials may be beneficial. In the case of polylactic acid (PLA), its biodegradable property [85] makes it attractive for triboelectric application in biomedical devices, or even from an environmentally sustainable point of view. Pan et al have reported biodegradable triboelectric NGs by pairing PLA with gelatin, with magnesium serving as the counter electrode, thus forming a device that is fully degradable in water within 40 d [93]. Their initial investigation showed low charge density generated by the contact electrification from smooth gelatin and PLA films, leading to an optimized design where the surface roughness was enhanced in accordance with previously reported surface morphology-modified designs [94, 95].

Membranes with high surface area were made by incorporating PLA electrospun nanofibers, instead of PLA films. The electrospinning was conducted by spraying PLA-acetone-chloroform mixed solution at a distance of 20 cm against Mg foil, under a DC voltage of 15 kV. Thin films of gelatin with rough surfaces were made by drop casting and spin coating gelatin solution (in de-ionized water) on top of sandpaper. The film was then transferred to Mg electrode with the help of water soluble adhesive tape, with the rough surface of the gelatin exposed by peeling off the sandpaper. A schematic of the fabrication process of the two parts of the triboelectric NG is shown in figure 14(a), with surface SEM image shown in figures 14(b) and (c). Control tests were conducted to show that the triboelectric NG output improved when the polymer surfaces were nanostructured. Smooth PLA films and electrospun PLA membranes were each paired against smooth and rough gelatin films in all possible combinations, showing that the largest open circuit voltage and short-circuit current were generated from when pairing the PLA nanofiber membrane with rough gelatin film. A maximum output power density of 5 W m⁻² was demonstrated when using a PLA nanofiber membrane thickness of 60 µm (controlled by the duration of electrospinning). The authors pointed out that thinner membranes may have provided greater effective contact area, however, complete coverage of the surface by nanofibers was not possible. Fatigue testing of the as-fabricated triboelectric NG was conducted up to 15000 contacting cycles, showing only a slight decay of the open-circuit voltage output. The authors observed that the deterioration was caused partly due to the PLA nanofibers being lifted from their base and attached to the gelatin counter surface. To secure the PLA nanofibers in place, degradable glue could be used to minimize the deteriorating output characteristics.

The degradation characteristics of the NG were investigated by leaving individual parts from the NG submerged in a bath of natural spring water. Water in the bath was regularly refreshed and gently stirred while maintaining the pH at around 6.5 to mimic natural water systems. The degradation status of the three different components, including Mg foil, gelatin film attached on Mg foil, and PLA nanofiber attached on Mg foil, was monitored over time. Figure 15 shows series of the photos taken from this experiment [93], providing information over approximately 20 d during which all the parts were fully dissolved. Dissolving mechanism of gelatin and PLA can be found in [96–99]. Noticeably, the relatively large surface area of the PLA nanofiber membrane aided in the fast dissolution of PLA in water.

7. ZnO-polymer nanocomposite piezoelectric NG

Inorganic piezoelectric nanomaterials typically possess high piezoelectric coefficients, but are not often suitable NG applications due to their brittle nature [1, 3]. In order to improve mechanical stability, nanocomposite-based NGs comprising well-aligned piezoelectric ZnO NWs grown within flexible nanoporous polycarbonate (PC) templates matrix were fabricated using two different template-assisted
nanowire growth methods. In the first, Ou et al have reported a novel approach to grow robust solid ZnO NWs within flexible PC templates using a simple, scalable and low-temperature hydrothermal nano-synthesis method [64]. The synthesis consisted of two steps (figure 16(a)) that included (i) a seeding process inside the pores of the PC template using zinc nitrate and hexamethylenetetramine (HMTA) precursor solution followed with (ii) ZnO nanowire growth within the pores of PC template bathed in HMTA precursor in a teflon-sealed stainless steel autoclave reactor at 95 °C for 5h as the optimum growth conditions. Refreshing of the precursor was needed repeatedly in order to obtain higher density of long fully grown NWs. ZnO crystals formed on the surface of the PC template were removed by hydrochloric acid before each precursor refreshing step. The ZnO NWs could, by burning away the PC template at
500 °C for 0.5 h as shown in figure 16(b), reveal NWs with average diameter 256 ± 51 nm and length 8.4 ± 2.1 µm, which was quite close to the dimension of the pores in the PC template used (pore dimension: average diameter ~227 ± 92 nm and length ~12 µm). The ZnO NWs grown by this template-assisted synthesis route were found to have higher aspect ratio that when grown directly onto indium tin oxide (ITO)-coated substrates from the same precursor solution where the typical nanowire length achieved was ~4 µm with a large variation in nanowire diameters. However, the orientation and crystalline structure of the template-grown ZnO NWs were found to be different than those directly grown onto ITO-coated substrates as observed by XRD and high-resolution transmission electron microscopy (HRTEM). Figure 16(c) provides the XRD patterns of bare PC template, seeded PC template, and NWs grown in the template with and without refreshed precursor, showing that the template-grown ZnO NWs were polycrystalline. The observed dominant peak of (1 0 0) indicates that ZnO NWs exhibited an oriented a-axis growth along the [100] direction, resulting from stacks of individual grown single-crystalline nanoparticles with the preferential c-axis orientation vertical to the pore walls in the nanoconfined growth process. The polycrystalline ZnO NWs were formed due to fusing of the nanoparticles or nanorods together.

A second ZnO-PC nanocomposite synthesis method involved using a template-assisted electrodeposition (TAED) method [63] as reported by Boughey et al. As before, growth of NWs with preferred [100] axis orientation parallel to the axis of the ZnO NWs was achieved. However, unlike in the case of hydrothermal synthesis, the nanowire growth here was driven by an electric potential in the presence of aqueous electrolyte solution. A nanoporous PC template with nominal pore diameter around 200 nm, length around 12 µm was prepared by sputtering ~100 nm thickness Ag electrode on one side of its surface. The thin deposited Ag electrode performed as working electrode during electrodeposition and later as one of the charge collecting electrodes for NG application. The side of the template with electrode was further protected by polyimide film to prevent deposition onto the back surface. To conduct the deposition, a three-electrode system, which included the Ag working electrode, Pt counter electrode and Ag/AgCl reference electrode, was adopted in a 0.1 M Zn(NO₃)₂ solution (figure 17(a)). A potentiostat in chronocoulometry mode was used to supply a voltage of −1 V between working electrode and reference electrode for a deposition duration of ~15 min to accomplish a complete filling of the PC template nanopores with ZnO. Field-emission SEM (FE-SEM) was used to observe freed ZnO NWs (figure 17(b)) by dissolving the PC template with chlorobenzene.
followed by heat treatment to burn away the PC template in a furnace at 500 °C for 30 min. XRD analysis of ZnO NWs within the PC template (figure 17(c)) showed that the preferred orientation of the NWs is [100]. The presence of other peaks in figure 17(c) could be explained by the polycrystalline nature of the electrodeposited ZnO NWs, albeit with an overall preferred orientation. Alternatively, the NWs could have been formed of single crystallites with different orientations, but with the majority pointing along the same preferred orientation. Further HRTEM examination on a single freed ZnO nanowire (figure 17(d)) proved the growth direction of the NWs was along the [100] axis, which was parallel to the long axis of the nanowire, possibly due to a result of stacks of single crystallite nanoparticles piled on top of one another with their [002] axis parallel to the plane of the template.

The ZnO-PC nanocomposites fabricated by the template-assisted methods described above were subsequently incorporated into flexible piezoelectric NGs [63, 64]. In both cases, appropriate electrodes were applied on to the surfaces of the templates for charge collection from the piezoelectric ZnO NWs embedded within. The piezoelectric responses of these NGs were measured by using vibrational shakers similar to the one described in previous reports built by Whiter et al [21] (figure 7(c)). The electrical output characteristics of the NGs, namely open-circuit voltage, short-circuit current and peak power output across impedance-matched loads are compared in figure 18, with typical $V_{oc}$ between 50 to 500 mV, $I_{sc}$ between 10 to 30 nA across a range of low-level vibrating frequencies. Maximum power densities were achieved as high as ~1600 mW m$^{-3}$ for hydrothermally grown NG and ~150...
tested by continuous impacting that lasted for up to 540 000 cycles and 432 000 cycles, respectively, showing a reasonably constant output voltage throughout the entire test bar ring an initial ~10% drop within the first few hours of the test (figure 18), and negligible degradation in performance for over a period of 4 months. The PC template was found to provide a protective environment within which the ZnO NWs were securely embedded and aligned, leading to good fatigue performance. This is an important feature as ZnO often suffers from both mechanical and environmental degradation, which were mitigated here through the presence of the PC template. Fatigue data for ZnO-based NGs is not often reported, and hence these polymer-based nanocomposite NGs represent an advance in terms of durability and reliability of performance, which are key to any energy harvesting application.

8. Outlook

In this review, we have discussed several advantages of polymer-based NGs, including polymer-ceramic hybrid NGs, such as superior robustness, low-cost, flexibility, durability and in some cases biodegradability. Additionally, the ability to precise control crystalline phases in polymeric materials is likely to prove beneficial in developing next-generation NGs in the coming years. Recently there have been reports on NGs made from shape memory polymers, which provide recovery from large deformation [100] or even self-healing characteristics to cutting damage on NGs [101]. Although there are a few self-healing NGs reported based on nanostructured materials [102], most of the attempts remain focused on certain bulk polymers, and there may scope to extend such concepts to polymer-based nanocomposites in order to further increase the energy harvesting performance. Challenges also exist in the search for other polymeric candidates, including hybrid materials that may have better piezoelectric or triboelectric properties upon combination of different materials systems. For example, given the fact that many piezoelectric ceramics possess outstanding piezoelectric coefficients, it may be possible to embed ceramic nanoparticles within nano-polymeric matrices for improved polarisation effects. Doping in polymer NWs to achieve enhanced ferroelectric effect can be another approach for further improving polymer-nanowire based NGs. For example, it was reported that doping electrospun poly(vinylidene fluoride-hexafluoropropylene)(P(VDF-HFP))/graphene nanofibers with Eu3+ enhanced the crystallinity of the piezoelectric β phase of the polymer for sensing applications [103]. Other doping mechanisms, including the use of metallic inclusions, such as silver nanoparticles have also been reported [104]. Furthermore, future research of this field will benefit from progress in the discovery of new piezoelectric polymeric systems and crystalline phases, both synthetic and natural, that may find use in both piezoelectric and triboelectric energy harvesters, Cellulose, for example, is an abundant and common natural polymer can be found from cell walls of green plants, and it has recently been incorporated as piezo- or tribo-active materials for energy harvesting applications [105–108]. It is clear that advances in nanofabrication of polymeric materials and devices will likely continue to drive the field forward, particularly through precise control and/or enhancement of their relevant properties at the nanoscale.

Acknowledgments

S K-N is grateful for financial support from European Research Council through an ERC Starting Grant (Grant No. ERC-2014-STG-639526, NANOGEN). Q J is grateful for financial support through a Marie Sklodowska Curie Fellowship, H2020-MSCA-IF-2015-702868.

ORCID iDs

Qingshen Jing @ https://orcid.org/0000-0002-8147-2047
Sohini Kar-Narayan @ https://orcid.org/0000-0002-8151-1616

References

[1] Crossley S, Whiter R A and Kar-Narayan S 2014 Polymer-based nanopiezoelectric generators for energy harvesting applications Mater. Sci. Technol. 30 1613–24
[2] Cook-Chennault K A, Thambi N and Sastry A M 2008 Powering MEMS portable devices—a review of non regenerative and regenerative power supply systems with special emphasis on piezoelectric energy harvesting systems Smart Mater. Struct. 17 1–33
[3] Crossley S and Kar-Narayan S 2015 Energy harvesting performance of piezoelectric ceramic and polymer nanowires Nanotechnology 26 344001
[4] Wang Z L 2013 Triboelectric nanogenerators as new energy technology for self-powered systems and as active mechanical and chemical sensors ACS Nano 7 9533–57
[5] Fan F R, Tian Z Q and Lin Wang Z 2012 Flexible triboelectric generator Nano Energy 1 328–34
[6] Wang Z L, Chen J and Lin L 2015 Progress in triboelectric nanogenerators as a new energy technology and self-powered sensors Energy Environ. Sci. 8 2250–82
[7] Yang R, Qin Y, Dai L and Wang Z L 2009 Power generation with laterally packaged piezoelectric fine wires Nat. Nanotechnol. 4 34–9
[8] X U, Qin Y, Xu C, Wei Y, Yang R and Wang Z L 2010 Self-powered nanowire devices Nat. Nanotechnol. 5 366–73
[9] Wang Z L and Song J 2006 Piezoelectric nanogenerators based on zinc oxide nanowire arrays Science 312 242–6
[10] Chen X, Xu S, Yao N and Shi Y 2010 1.6 V nanogenerator for mechanical energy harvesting using PZT nanofibers Nano Lett. 10 2133–7
[11] Lu M P, Song J, Lu M Y, Chen M T, Gao Y, Chen L J and Wang Z L 2009 Piezoelectric nanogenerator using p-type ZnO nanowire arrays Nano Lett. 9 1223–7
[12] Huang C T, Song J, Lee W F, Ding Y, Gao Z, Hoo Y, Chen L J and Wang Z L 2010 GaN nanowire arrays for high-output nanogenerators J. Am. Chem. Soc. 132 4766–71
Zhao L, Zheng Q, Ouyang H, Li H, Yan L, Shi B and Li Z 2016 A size-unlimited surface microstructure modification method for achieving high performance triboelectric nanogenerator Nano Energy 28 172–8

Sun J G, Yang T N, Kuo I S, Wu J M, Wang C Y and Chen L J 2017 A leaf-molded transparent triboelectric nanogenerator for smart multifunctional applications Nano Energy 32 180–6

Lyu S, Sparer R and Untereker D 2005 Analytical solutions to mathematical models of the surface and bulk erosion of solid polymers J. Polym. Sci. B 43 383–97

Tamada J A and Langer R 1993 Erosion kinetics of hydrolytically degradable polymers Proc. Natl Acad. Sci. USA 90 552–6

Kim K, Yu M, Zong X, Chiu J, Fang D, Seo Y S, Hsiao B S, Chu B and Hadjijargyrou M 2003 Control of degradation rate and hydrophilicity in electrosyn non-woven poly(D,L-lactide) nanofiber scaffolds for biomedical applications Biomaterials 24 4977–85

Gorgieva S and Kokol V 2011 Collagen-versus gelatine-based biomaterials and their biocompatibility: review and perspectives Biomater. Appl. Nanomed. (https://doi.org/10.5772/24118)

Liu R et al 2018 Shape memory polymers for body motion energy harvesting and self-powered mechanosensing Adv. Mater. 30 1705195

Xu W, Huang L B and Hao J 2017 Fully self-healing and shape-tailorable triboelectric nanogenerators based on healable polymer and magnetic-assisted electrode Nano Energy 40 399–407

Chen D, Wang D, Yang Y, Huang Q, Zhu S and Zheng Z 2017 Self-healing materials for next-generation energy harvesting and storage devices Adv. Energy Mater. 7 1700890

Adhikary P, Biswas A and Mandal D 2016 Improved sensitivity of wearable nanogenerators made of electrosyn Eu3+ doped P(VDF-HFP)/graphene composite nanofibers for self-powered voice recognition Nanotechnology 27 495501

Mandal D, Henkel K and Schmeißer D 2014 Improved performance of a polymer nanogenerator based on silver nanoparticles doped electrosyn P(VDF–HFP) nanofibers Phys. Chem. Chem. Phys. 16 10403

Alam M M and Mandal D 2016 Native cellulose microfiber-based hybrid piezoelectric generator for mechanical energy harvesting utility ACS Appl. Mater. Interfaces 8 1555–8

Zhang G, Liao Q, Zhang Z, Liang Q, Zhao Y, Zheng X and Zhang Y 2015 Novel piezoelectric paper based flexible nanogenerators composed of BaTiO3 nanoparticles and bacterial cellulose Adv. Sci. 3 1500257

Zheng Q, Zhang H, Mi H, Cai Z, Ma Z and Gong S 2016 High-performance flexible piezoelectric nanogenerators consisting of porous cellulose nanofibril (CNF)/poly(dimethylsiloxane) (PDMS) aerogel films Nano Energy 26 504–12

Cui P, Parida K, Lin M F, Xiong J, Cai G and Lee P S 2017 Transparent, flexible cellulose nanofibril-phosphorene hybrid paper as triboelectric nanogenerator Adv. Mater. Interfaces 4 1700651