Piezoelectric Microstructured Fibers via drawing of multimaterial preforms
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ABSTRACT
We report an all-polymer flexible piezoelectric fiber that uses both judiciously chosen geometry and advanced materials in order to enhance fiber piezoelectric response. The microstructured/nanostructured fiber features a soft hollow polycarbonate core surrounded with a spiral multilayer cladding consisting of alternating layers of piezoelectric nanocomposites (polyvinylidene enhanced with BaTiO3, PZT or CNT) and conductive polymer (carbon filled polyethylene). The conductive polymer layers serve as two electrodes and they also form two spatially offset electric connectors on the fiber surface designed for the ease of connectorization. Kilometer-long piezoelectric fibers of submilimeter diameters are thermally drawn from a macroscopic preform. The fibers exhibit high output voltage of up to 6V under moderate bending, and they show excellent mechanical and electrical durability in a cyclic bend-release test. The micron/nano-size multilayer structure enhances in-fiber poling efficiency thanks to the small distance between the conducting electrodes sandwiching the piezoelectric composite layers. Additionally, spiral structure greatly increases the active area of the piezoelectric composite, thus promoting higher voltage generation and resulting in 10-100 higher power generation efficiency over the existing piezoelectric cables. Finally, we weave the fabricated piezoelectric fibers into technical textiles and demonstrate their potential applications in power generation when used as a sound detector and a wearable textiles.

Keywords: Flexible piezoelectric fibers; piezoelectric generators; energy harvesting fibers; BTO-PVDF fibers; PZT-PVDF fibers

1. INTRODUCTION

Over the past decade, significant effort has been put into the R&D of energy harvesting and conversion devices that operate based on piezoelectric effect [1-4]. Unlike the energy harvesters utilizing solar or thermal energy, performance of piezoelectric generators is generally not limited by the environment factors. An important driving force for developing novel piezoelectric energy generators is the growing popularity of the personal wearable electronics such as on-garment displays, wearable sensors in sports and medicine, virtual-reality devices, and smart watches and bracelets [5-9]. In these devices, piezoelectric generators or transducers utilizing mechanical energy from human body motions could be used as power sources or sensor components. Another emerging field where piezoelectric generators could find niche applications relates to the self-energized electronics for automotive or aerospace industries. Piezoelectric generators harvesting energy from the traffic-induced vibrations or other parasitic mechanical movements motions could power on-board electronic systems such as wireless sensor networks (WSNs) with low-power consumption [10, 11]. Note that for these applications, piezoelectric generators in the form of fibers or strips are highly desired [12], as thanks to their flexibility, they could be woven seamlessly into multifunctional fabrics for wearable or on-board applications, or, alternatively, coiled into compact energy generation cells.

Many attempts have been made to fabricate piezoelectric fibers. A simple method is directly depositing or wet-extruding ceramic piezoelectric materials such as ZnO nanowires (NWs), BaTiO3 (BTO) NWs and Pb(Zr0.52Ti0.48)O3 (PZT) NWs along a metallic wire/filament [13-17]. For instance, Qiu et al. reported a piezoelectric fiber fabricated by extruding a mixture of PNN-PZT powder and organic solvent along a Pt wire [13]. Wang and coworkers proposed a ZnO-based piezoelectric fiber fabricated by growing ZnO-NWs on an Au-coated Kevlar fiber using a hydrothermal method [14]. Note that the mechanical reliability of these piezoelectric fibers could be problematic, since frequent bending and surface abrasion would make the ceramic materials cracking and even peeling off from the fiber core. To improve robustness of the fibers, Wang and co-workers have proposed to cover the base of ZnO NWs with a protective polydimethylsiloxane (PDMS) layer using a method combining surface-coating and plasma-etching [16]. Instead of depositing piezoelectric...
layers onto a fiber/wire substrate, fabrication of piezoelectric fibers directly from piezoelectric polymers constitutes an alternative option. Compared to ceramic materials, piezoelectric polymers generally have better flexibility, thus they are more suitable for wearable applications. Among all of the piezoelectric polymers, poly(vinylidene fluoride) (PVDF) and poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE) are predominantly utilized in piezoelectric devices due to ease of their thermal processing, high flexibility, high strain level and good piezoelectric properties [4]. Lund et al. used the melt-spinning method to fabricate a bicomponent fiber that had a PVDF sheath and a carbon-black impregnated polyethylene (CB-PE) core serving as the inner electrode [18, 19]. Using the same method, Roth et al. reported a piezoelectric fiber that had a PVDF sheath and carbon-nanotube impregnated polypropylene (CNT-PP) core [20]. Recently, Liu et al. adopted an electrowetting-aided dry spinning method to fabricate a piezoelectric fiber featuring a metallic core covered by a thin PVDF or PVDF-TrFE layer [21]. Piezoelectric fibers produced via the traditional spinning methods typically adopt a simple core-sheath structure, and the as-spun fibers may require an additional deposition of a metallic layer as an outer electrode that may have reliability issues due to surface abrasion and repeated bending or stretching actions. Also note that for PVDF piezoelectric fibers, high-voltage poling of the PVDF layers has to be performed during (or after) the spinning process in order to promote the nonpolar α to the ferroelectric β phase transition. In addition to electric poling of PVDF, one also uses stretching during poling process, thus further complicating the fabrication process. PVDF-TrFE, on the other hand, could spontaneously crystallize into β phase during its solidification during a spinning process; however, compared to PVDF, the price of PVDF-TrFE is considerably higher.

Piezoelectric polymer fibers could be also fabricated using the fiber drawing technique. In this method, a geometrically complex multimaterial fiber preform with a length of tens of centimeters is first assembled using stacking of tubes, rods, multilayered films, or other functional components. Then, the preform could be drawn into fibers using a fiber drawing tower (Figure 1a). Geometry of the resultant fibers depends on parameters in the drawing process such as the temperature distribution in a furnace, the fiber drawing speed and the preform feed velocity, pressurization of the preform, as well as application of the electromagnetic fields. Fibers drawn from a macroscopic preform would generally retain the preform structure; however, sizes of the constituent elements will be reduced to micro- or even nano-scale. Therefore, various geometrically complex transverse structures that considerably enhance the fiber functionality could be realized within a fiber on a sub-micron scale by engineering the preform structure on a macroscopic scale and optimizing the conditions of the fiber drawing process. This, generally, cannot be accomplished by traditional fiber-spinning methods such as melt-spinning [22], or wet-spinning [23, 24]. As an example, Egusa et al. demonstrated a multimaterial piezoelectric fiber using the fiber drawing technique [25]. This piezoelectric fiber featured a PVDF-TrFE piezoelectric layer sandwiched between two conductive polycarbonate (CPC) electrode layers and assembled with Tin microfilaments for electrical connection. The fiber also had an outermost isolating PC layer serving as the protective cladding. An acoustic transducer was developed based on this fiber, and showed a good response to acoustic waves with frequencies from kilohertz to megahertz. The fiber had several limitations, as it used very expensive PVDF-TrFE material, and it integrated in its structure a Tin metallic microfilament, thus reducing the fiber reliability with respect to flexing. Finally, connecting to such fibers is challenging, as it requires manipulation with built-in micron-sized metallic electrodes. In Ref. [26] it was proposed that spontaneous piezoelectricity can be achieved in PVDF nanoribbons, when using consecutive re-drawings of the same fiber under high voltage. The authors claimed that under such conditions PVDF could crystallize into an exotic piezoelectric γ phase. At this point, it is difficult to evaluate the robustness of this fabrication technique, as there were no further reports of using this fabrication method. Additionally, multiple re-drawing of the same fiber is needed for fabrication of PVDF nanoribbons, which could be labor intensive and of low yield. To improve the piezoelectric properties of the drawn fiber, while avoiding using expensive PVDF-TrFE, a PVDF impregnated with ceramic piezoelectric materials such as BTO and PZT could be used instead [27-29]. Although a higher concentration of the ceramic fillers generally results in enhanced piezoelectric performance of PVDF, it would at the same time decrease the polymer viscosity [25], thus eventually leading to capillary break-up of the fiber during drawing. Thus, the maximal concentration of ceramic fillers is limited by the drawing process. Furthermore, CNTs could be also impregnated into PVDF in order to enhance its piezoelectric properties via spontaneous formation of the β phase crystals in PVDF [30-31]. Incorporation of a small amount of CNTs can lead to remarkable improvements of the electrical and mechanical properties of the PVDF fibers. There, the authors argued that application of a shear stress to the polymer melt leads to the preferred orientation of the macromolecules, thus reducing the entropy of the polymer melt and leading to the flow-induced crystallization from the melt. Moreover, incorporation of CNTs can promote the shear-induced crystallization behavior and enhance the formation of β-crystals in PVDF nanocomposites. Also, the CNTs could induce charge accumulation at the interface during electrical poling process, thus further promoting the conversion
of the PVDF molecules’ α-phase into the β-phase [30-31]. Similar to the case of ceramic fillers, the maximum concentration of CNTs is also limited by the fiber drawing process.

In this paper, we report fabrication of the multimaterial piezoelectric fibers from perovskite ceramic nanoparticles (BTO/PZT)-PVDF, and CNT-PVDF composites via fiber drawing. Furthermore, we perform a comparative study of the piezoelectric performance of thus fabricated fibers. The proposed fibers feature a novel spiral geometry that significantly increases the fiber piezoelectric response. Due to the judicious arrangement of the conductive layers, connecting to our fibers is easy as the two electrodes occupy the opposite sides of the exposed fiber surface. The use of conductive plastic composite electrodes also increases the fiber reliability. The proposed piezoelectric fibers feature a soft hollow PC core surrounded by a multilayer cladding consisting of the alternating sub-micron-sized piezoelectric/electrode layers as shown in Figure 1d. PVDF, due to its low cost and availability is chosen as the principle component in the piezoelectric layers, while perovskite ceramic (BTO or PZT) nanoparticles or CNTs are impregnated into PVDF layers in order to enhance their piezoelectric properties. This approach allows replacement of expensive PVDF-TrFE material, while resulting in the comparable or even superior piezoelectric response. The carbon-impregnated low density polyethylene (C-LDPE) layers serve as electrode layers. By bending or stretching the fibers, piezoelectricity could be effectively generated. Experimentally, a piezoelectric generator using a 10 cm long BTO-PVDF (BTO concentration: 20 wt%) fiber could generate an open-circuit voltage of 1.4 V and a short-circuit current of 0.8 nA respectively, when the fiber tip is displaced transversely by 10 mm. The corresponding voltage and current were ~6 V and ~4 nA for a PZT-PVDF (20 wt% PZT) fiber generator, and ~3 V and ~1.2 nA for a CNT-PVDF (0.4 wt% CNT) fiber generator. Compared to the previous piezoelectric fibers reported in Refs [14, 18-21], our fibers adopt a spiral structure, and thus have much larger active areas for piezoelectricity generation as well as smaller gaps between the electrodes. As a result, our fibers could generate much higher piezoelectric currents, which are proportional to the number of turns in a spiral. Among other advantages of the piezoelectric fibers reported in this paper is low cost of the materials used in fabrication, light weight, good durability, and possibility of mass production via fiber drawing. As examples of practical applications of the proposed piezoelectric fibers, we present energy harvesting textiles using BTO-PVDF fibers, and characterized their performance in the context of wearable microgenerators. Moreover, we also present detection of sound using CNT-PVDF fiber that feature piezoelectric voltage generated by sound wave to be proportional to the square root of the acoustic power.

2. RESULT AND DISCUSSION

2.1 Fabrication of the Piezoelectric Micro/Nano-Structured Fibers

Figure 1 summarizes the fabrication process of a piezoelectric fiber. A fiber preform is assembled by co-rolling two PVDF-based piezoelectric mats (thickness: 100 μm) sandwiched between two C-LDPE films (thickness: 85 μm, volume resistivity: 2.2 Ω*m, Bystat International Inc.) around a hollow PC tube (diameter: 25.4 mm, McMaster Carr) (Figure 1b, c). The above-mentioned polymer materials are chosen for fiber fabrication because they have similar processing temperatures which is important for co-drawing. The conductive layers are spatially offset in order to produce two easily accessible electrodes on the preform surface after rolling the preform. The piezoelectric mats (Figure 1f) used in the preform are BTO-PVDF, PZT-PVDF, or CNTs-PVDF nanocomposites, which were fabricated in-house via electrospinning. Besides, we also varied the concentrations of BTO and CNTs in the mats to study how they would affect the piezoelectric properties of the fabricated fibers. After assembly, the preforms were drawn into piezoelectric fibers using a plastic fiber drawing tower. During fiber drawing, we also explored applications of high voltage (up to 5 kV) to the preform electrodes in order to pole the drawn fibers directly during fabrication process. We found that while this only led to a modest improvement in the piezoelectric functionality of the drawn fibers, (since the poling time is insufficient to provide a significant effect), using high voltage we could effectively control thickness of the layers in the piezoelectric fibers. This is because the conductive electrode layers in a softened preform have a tendency to attract to each other under voltage application, and, thus, very thin (sub 1 μm) piezoelectric layers could be drawn. In Figure 1d, we show a typical cross section of the piezoelectric fiber (diameter: ~900 μm). The multilayer structure in the fiber cladding maintained well during drawing, while thicknesses of the individual piezoelectric or conductive layers typically ranged from 5 to 10 μm. For those fibers drawn under 5 kV, the fiber diameters were reduced to ~300 μm, and thickness of the piezoelectric layers or conductive layers could be less than 1 μm (Figure 1g). Finally, in order to further enhance the fibers’ piezoelectric property, they were poled in a silicone oil bath (80 °C) using a voltage of 1 kV for 12 hours. The poling voltage was then increased to 5 kV for 12 hours and finally 9 kV for 12 hours. The poled fibers were then utilized for development of various piezoelectric generator and energy generation systems.
2.2 Characterization of piezoelectric fibers

In order to characterize fiber piezoelectric properties, we use the following testing method. The two ends of a piezoelectric fiber (length: 10 cm, diameter: ~1mm) were glued to two C-LDPE strips as shown in Figure 2a and 2b. Note that, by design the fiber features two exposed electrodes positioned on the opposite sides of the fiber surface (see Figure 1c). Thus, before the connection, the piezoelectric fiber should be placed in a specific position: one fiber electrode is on the top while the other fiber electrode is on the bottom (this can be achieved by rotating the fiber). Then, one C-LDPE strip was attached to the top side of the fiber, while the other one was attached to the bottom side of the
fiber on the opposite end. In this way, the two strips would connect to the two different electrodes of the fiber. The piezoelectric fiber together with the C-LDPE strips were immobilized onto a 10 cm long, 1 mm thick PS substrate using Kapton tape. Due to asymmetry in the test cell structure, bending of the PS substrate would lead to a non-zero average strain in the piezoelectric fiber. Experimentally, one end of the PS substrate was fixed, while the other end was horizontally displaced by a micropositioning stage, thus bending the fibers (Figure 2c). The generated voltage and current of the piezoelectric fiber were measured using an Ivium Electrochemical Workstation (Ivium Technologies).

![Figure 3](image_url)

- **Fig.3** (a) Open-circuited voltage generated by a 10 cm long BTO-PVDF fiber with the BTO concentration of 5, 10, 15, 20, and 25 wt% subjected to a 1-cm displacement. (b-c) Comparison of the piezoelectric voltages generated by the poled BTO-PVDF fiber generator and the unpoled one. (d) and (e) show the open-circuit output voltage and short-circuit current generated by a 10 cm-long BTO-PVDF fiber generator (20 wt% BTO in the BTO-PVDF composite) when its moving end is displaced by 5, 10, 15, and 20 mm. (f-g) A durability test for the 10 cm long BTO-PVDF fiber (20 wt% BTO in BTO-PVDF composite) by continuously repeating 1 cm amplitude bend-release movements for 3 days. The open-circuit voltage and short-circuit current generated in a 1000 s period at the beginning of the first day (f) and at the end of the third day (g) are shown.

We first study the open-circuited voltage generated by the BTO-PVDF fiber generator as a function of the BTO concentration. As the concentration of BTO in the BTO-PVDF layer increased from 5 wt% to 25 wt%, the piezoelectric voltage of a fiber generator with its moving end displaced by 10 mm increased from ~0.15 V to ~2.5 V (Figure 3a). We find that drawing fibers with BTO concentrations higher than 25 wt% is challenging, because at such high BTO concentrations the viscosity of a BTO-PVDF composite is lowered significantly, thus resulting in capillary break-up during fiber drawing. Therefore, to maintain a stable fiber drawing while maximizing piezoelectric functionality, an optimal BTO concentration of 20 wt% was adopted in all our drawings. In Figure 3d and 3e, we find that when the moving end of the fiber was displaced by 5 to 20 mm, the corresponding open-circuit voltage increased from ~ 1 to ~1.7 V, and the short-circuit current increased from ~ 0.7 to ~1.3 nA. Besides, we note that the poling process plays major role in the functioning of the piezoelectric fibers. The fibers without poling exhibit an open-circuit voltage of ~1.5 mV, which is three orders of magnitude smaller than that of their poled counterparts (Figure 3b, c). A durability test was also conducted for fiber-based generators by continuously repeating the bend-release movements for 3 days. We find that the...
piezoelectric voltage and current generated by a fiber does not show degradation signs after the entire test that comprise ~26000 bend/release cycles (Figure 3f, g).

Next, piezoelectric generators based on PZT-PVDF piezoelectric fibers were studied. The advantage of PZT over BTO is its higher piezoelectric constant. We find that when the moving end of a PZT-PVDF (PZT concentration: 20 wt%) fiber generator is displaced by 10 mm, it generates an open-circuit voltage of ~6 V and short-circuit current of ~ 4 nA, which are ~4 times higher than those generated by BTO-PVDF fibers (Figure 4a, b). However, due to the high toxicity of PZT, PZT-PVDF fibers are probably not suitable for wearable applications.

Fig. 4 (a) and (b) show the open-circuit voltage and the short-circuit current generated by a 10 cm-long PZT-PVDF fiber generator (20 wt% PZT in the PZT-PVDF composite), when its moving end is displaced by 10 mm.

Piezoelectric generators based on CNT-PVDF fibers were assembled following the same procedures described before. We first studied the dependence of the voltages generated by the CNT-PVDF fibers on CNT concentrations. As shown in Figure 5b, when the moving end of the fiber generators was displaced by 10 mm, the 10-cm long CNT-PVDF fiber generator containing 0.1 wt% CNT generated an open-circuit voltage of ~0.8 V, while the generator containing 0.6 wt% CNT generated an open-circuit voltage of as high as ~6.8 V. We, furthermore, find that the fibers with CNT concentrations higher than 0.6 wt% are challenging to fabricate, as they tend to break up during the drawing process. Thus, we adopted an optimal CNT concentration of 0.4 wt% for all our CNT-PVDF fibers that guaranteed the ease of drawing while maintaining high generated voltage. The Figure 5c, d show that when the moving end of the CNT-PVDF (0.4 wt% CNT) fiber generator was displaced by 5 to 20 mm, the open-circuit voltage increased from ~ 1.7 to ~3.7 V, and the short-circuit current increased from ~0.2 to ~0.7 nA. From this we conclude the performance of the CNT-PVDF (0.4 wt% CNT) fiber generator is comparable to that of the BTO-PVDF (20 wt% BTO) fiber generator.

Fig. 5. (a) Photo of a CNTs/PVDF fiber generator. (b) Open-circuit voltage of a 10-cm long CNT-PVDF fiber generators with CNT concentrations of 0.1, 0.2, 0.4 and 0.6 wt% under 10 mm displacement. (c) and (d) show the open-circuit voltage and short-circuit current of a 10-cm long CNT-PVDF fiber (CNT concentration: 0.4 wt%), when the moving end of the fiber was displaced by 5, 10, 15, 20 mm.
3. EXAMPLES OF APPLICATIONS OF PIEZOELECTRIC FIBERS

![Fig. 6](image)

Fig. 6 (a) Schematic and a photo (b) of experimental setup of the underwater ultrasound detection using a CNT-PVDF fiber. (c) Piezoelectric voltages generated by the fiber, when the source acoustic powers were 2 W, 4 W and 6 W. (d) Square of the piezoelectric voltage generated by the generator has a linear relation with the acoustic power. The error bar is calculated by the standard deviation (SD) of the peak value of measured pulses.

**Stand-off Distributed Sound Detection.** We investigate performance of the sound-driven fiber generator under water. Experimentally, the two ends of a 10 cm long CNT-PVDF fiber were fixed in a water tank with a dimension of 60 cm × 28 cm × 15 cm (Figure 6). An ultrasonic probe was also immersed under water to emit ultrasound waves with a frequency of ~20 kHz. The distance between the probe and the fiber was ~ 20 cm. While the sonication was repeated with a period of 6 s (1 s on, 5 s off), the piezoelectric voltage generated by the fiber was continuously measured. As the power of the ultrasound wave increased, the amplitude of voltage generated by the CNT-PVDF fiber also increased (Figure 6c, d) according to $V^2 \sim P/f$ [32]. We note that in Figure 6c the generated voltage does not return to zero as the off time (5 s) is too short for all the water oscillations in the tank to subside. Normally, the off time should be longer than a minute to see the generation voltage to approach zero value.
Textile-based Piezoelectric Generators Woven using BTO-PVDF Fibers. Here, we present a prototype of the flexible, textile-base piezoelectric generators. It was fabricated using individual piezoelectric BTO-PVDF fibers and a classic Dobby-loom weaving process (Figure 7 a, b). We demonstrate that such textile generators could be potentially used as tactile or motion sensors for sport outfits or medical apparels. In this prototype, four 20 cm-long BTO-PVDF fibers (20 wt% BTO in BTO-PVDF composites) were weaved into a textile and then connected in series. The textile was then tightly wrapped around a human elbow (Figure 7c). In a 90 degree bend-release action of the elbow, the piezoelectric textile could generate open-circuited voltages of up to ~10 V and short-circuit currents of 5-15 nA (Figure 7d, e).

4. CONCLUSIONS

In summary, we have studied several material combinations, novel piezoelectric fiber designs and novel manufacturing techniques that allow fabrication of piezoelectric fibers with greatly enhanced piezoelectric properties compared to the existing counterparts. The micro/nano-structured piezoelectric fibers presented here feature a soft hollow PC core surrounded by a multilayer cladding consisting of alternating PVDF-based nanocomposite layers and conductive (C-LDPE) layers. We have also performed comparative study of three material combinations. A BTO/PVDF microstructured fiber (10 cm long; BTO concentration: 20 wt%) could generate an open-circuit voltage of 1.4 V and a short-circuit current of 0.8 nA, when the moving end of the generator was displaced transversely by 10 mm. The corresponding voltage and current were ~6 V and ~4 nA for a PZT-PVDF (20 wt% PZT) fiber generator, and ~3 V and ~1.2 nA for a CNT-PVDF (0.4 wt% CNT) fiber generator. Perovskite ceramics (such as BTO and PZT) could improve the fiber performance owing to their high piezoelectric coefficient. On the other hand, CNTs could induce the crystallization of polar phase in PVDF layers, thus leading to remarkable improvements in piezoelectric performance.
Also we note in passing that the CNTs/PVDF microstructured fibers are easier to draw to smaller diameters and they appear to have better mechanical flexibility. The resultant fibers exhibit excellent durability with high piezoelectric voltages (of up to 6 V) in a cyclic bend-release test (greater than 26000 cycles). Finally, we have present several examples of the practical applications of the proposed piezoelectric fibers: for distributed stand-off sound detector using CNT-PVDF fibers, and for energy harvesting using textile-based piezoelectric generators that incorporate BTO-PVDF fibers.

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