ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de

Wearable Energy Generating and Storing Textile Based on Carbon Nanotube Yarns

*Tae Jin Mun, Shi Hyeong Kim, Jong Woo Park, Ji Hwan Moon, Yongwoo Jang, Chi Huynh, Ray H. Baughman, and Seon Jeong Kim**

The challenges of textiles that can generate and store energy simultaneously for wearable devices are to fabricate yarns that generate electrical energy when stretched, yarns that store this electrical energy, and textile geometries that facilitate these functions. To address these challenges, this research incorporates highly stretchable electrochemical yarn harvesters, where available mechanical strains are large and electrochemical energy storing yarns are achieved by weaving. The solid-state yarn harvester provides a peak power of 5.3 W kg^{-1} for carbon nanotubes. The solid-state yarn supercapacitor provides stable performance when dynamically deformed by bending and stretching, for example. A textile configuration that consists of harvesters, supercapacitors, and a Schottky diode is produced and stores as much electrical energy as is needed by a serial or parallel connection of the harvesters or supercapacitors. This textile can be applied as a power source for health care devices or other wearable devices and be self-powered sensors for detecting human motion.

1. Introduction

Both for powering external devices and for powering sensors that monitor body movement and body function, there is a great interest in textiles that can harvest and store electrical energy.[1–4] Recently reported yarn supercapacitors and yarn batteries provide the flexibility and stretchability needed for textile applications.[1,5–18] Interesting progress has also been made on non-fiber type high performance triboelectric and piezoelectric harvesters that respond to either an applied pressure or the stretch-induced sliding between the harvester surfaces.[1,19–21] A few types of stretchable triboelectric and stretchable piezoelectric harvester fibers have been reported,[22–24] but these harvesters have not yet provided a competitive performance.

The only harvesters capable of generating high power by solely the tensile deformation of a fiber are based on stretch-induced changes in the yarn capacitance. Of these capacitance change yarns, those utilizing stretch-induced changes in the dielectric capacitance have the disadvantage of requiring up to thousands of volts of an applied bias voltage. Hence, we presently used so-called "twistron" mechanical energy harvesters, which require no applied bias voltage.[25]

The twistron harvesters can convert tensile or torsional mechanical deformations directly into electrical energy without the need for a bias voltage. Furthermore, since these electrochemical twistron harvesters are flexible, mechanically robust yarns, they can be easily woven into textiles and configured in textiles in series or in parallel arrangements to increase either the output voltage or output current. Another advantage of this type of harvester is that this twistron harvester can be a self-powered strain sensor itself. Unlike other mechanical energy harvesters, such as triboelectric or piezoelectric harvesters, we can use strain-induced voltage change to harvest energy linearly like a strain sensor.[25,26]

Since the twistron yarn harvesters are electrochemical devices, two electrodes are required. To maximize the output power by minimizing the electrochemical impedance, these two electrodes are placed in close proximity. In fact, both electrodes are in the same yarn of the woven textiles. In the harvester yarns, we will use a homochiral yarn (a yarn having the same handedness of twisting and coiling) as one electrode and a heterochiral yarn (a yarn having different handedness of twisting and coiling) as the second electrode. The benefit of using such electrodes is that both electrodes can contribute to energy harvesting, since the changes in the electrode voltage are in opposite directions for stretching a homochiral and a heterochiral yarn. Furthermore, contrary to a previous reported twistron harvester that charged only a commercial capacitor, we

T. J. Mun, J. W. Park, J. H. Moon, Prof. Y. Jang, Prof. S. J. Kim
Center for Self-Powered Actuation
Department of Biomedical Engineering
Hanyang University
Seoul 04763, South Korea
E-mail: sjk@hanyang.ac.kr

Dr. S. H. Kim
Research Institute of Industrial Technology Convergence
Korea Institute of Industrial Technology
Ansan-si 15588, South Korea

Dr. C. Huynh
Lintec of America
Nano-Science & Technology Center
Richardson, TX 75081, USA

Prof. R. H. Baughman
Alan G. MacDiarmid Nano Tech Institute
University of Texas at Dallas
Richardson, TX 75080, USA

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.202000411.

DOI: 10.1002/adfm.202000411

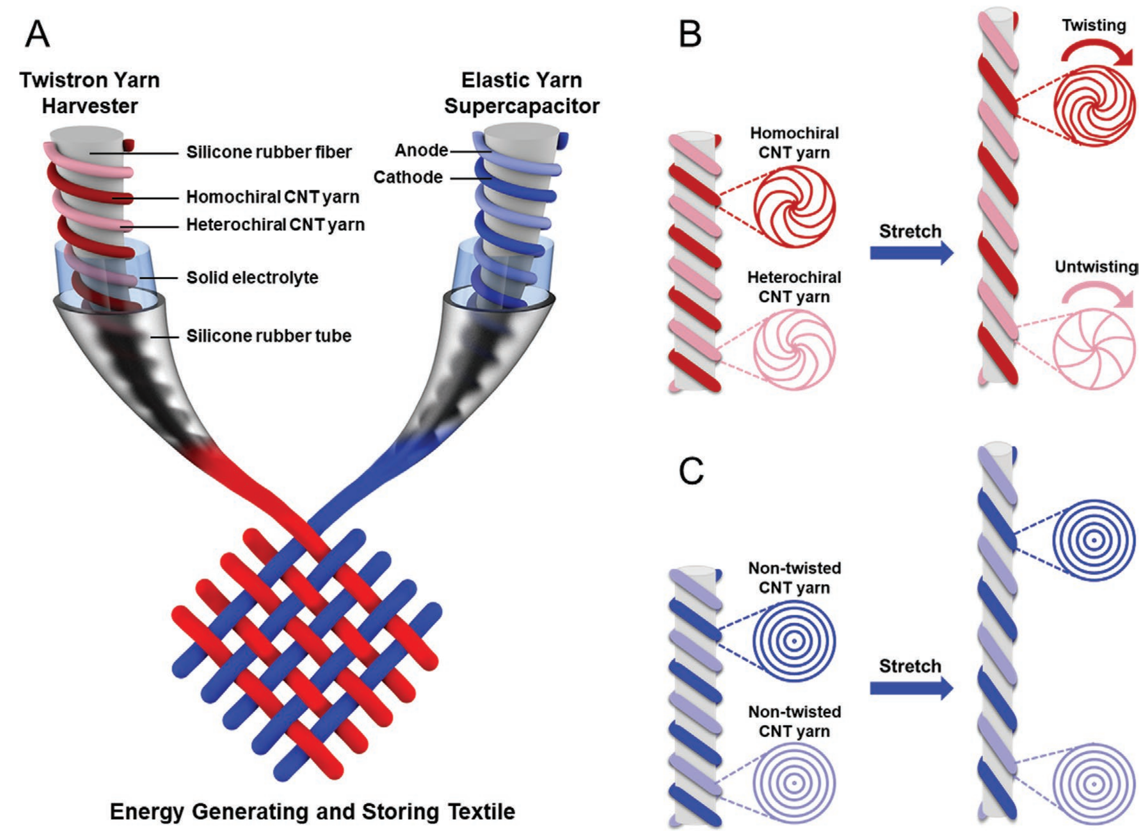

Figure 1. Scheme of energy generating and storing textile, and principle of energy harvester and supercapacitor based on carbon nanotube (CNT) yarn twist. A) Configuration of energy generating and storing textile that consists of one-body twistron yarn energy harvester, elastic yarn supercapacitor. Harvester and supercapacitor including the two CNT yarn, silicone rubber fiber and solid electrolyte in silicone rubber tube. B) Energy harvester consist of homochiral CNT yarn and heterochiral CNT yarn. When stretching the harvester, homochiral CNT yarn is twisted, and heterochiral CNT yarn is untwisted respectively. C) Supercapacitor consists of two non-twisted CNT yarns for anode and cathode. When stretching the supercapacitor, both non-twisted CNT yarns are constant.

will charge a supercapacitor consisting of one package textile during energy harvesting. **Figure 1**A illustrates the configurations used for the harvester yarns and the supercapacitor yarns as well as their arrangement into textiles. To stabilize the harvester and supercapacitor yarns with respect to moisture loss from the electrolytes, each of these yarns is incorporated in a hollow silicone rubber fiber.

2. Result and Discussion

2.1. The Solid-State Yarn Energy Harvester

The carbon nanotube (CNT) yarns were produced by drawing sheets of aligned carbon multiwalled nanotubes (MWNTs) from forests[27] and then inserting twists to transform the sheets into either twisted or coiled yarns. The CNT yarns used to make the energy harvesters and supercapacitors were of two types. Unless otherwise specified, a 30-cm-long, 4.5-cm-wide CNT sheet stack containing 15 layers was used as the precursor. For application in the twistron energy harvesters shown in Figure 1B and Figure S1A (Supporting Information), the twistron yarns were made for the fabrication of the heterochiral and homochiral yarns by wrapping the yarns around a stretched silicone rubber fiber core. These twistron yarns were highly twisted up to the point of coil initiation by inserting 2000 turns m^{-1} of twist. Although these yarns have a high electrical conductivity, the twistron harvester performance was enhanced by plying the harvester yarns with a 25-µm-diameter platinum wire. In the case of the homochiral yarns, yarns highly twisted with Pt wire, whose direction of twist insertion was clockwise and diameter was 125 µm, were wrapped with the same clockwise direction around a 250-µm-diameter silicone rubber fiber that was stretched by 300%. Otherwise, in the case of the heterochiral yarns, yarns highly twisted with Pt wire, whose direction of twist insertion was counterclockwise and diameter was ≈125 µm, were wrapped with the clockwise direction (the opposite direction of the twisted insertion) around the same rubber fiber. For applications in supercapacitors, as shown in Figure 1C and Figure S1B (Supporting Information), where the inserted twist undesirably decreases the capacitance, a non-twisted yarn was prepared by inserting ≈10 turns cm^{-1} of twist to convert the CNT sheet stack into a twisted yarn and then removing this same amount of twist. Both the anode and cathode electrodes were prepared by the same non-twisted CNT yarns, which were wrapped parallel around the 300% stretched silicone rubber fiber(250-µm-diameter).

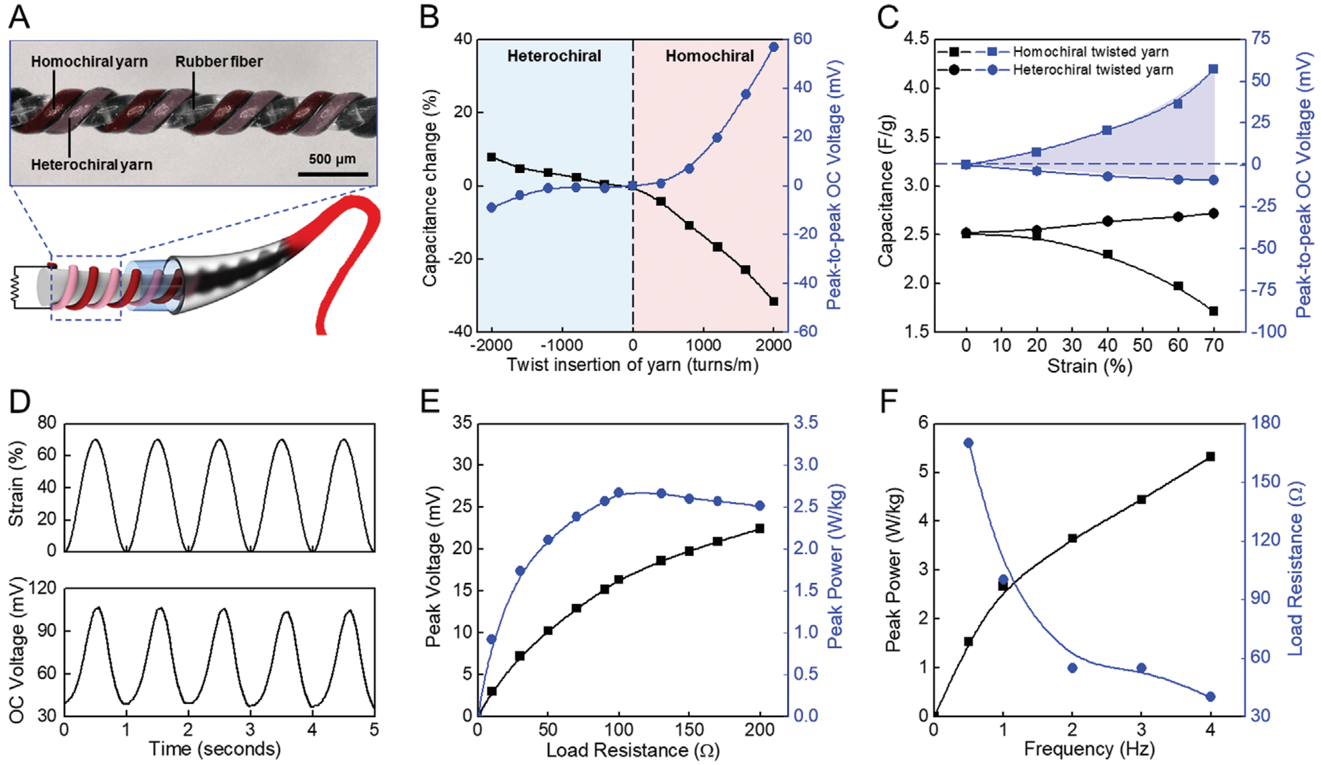

Figure 2. Characterization of twisted CNT yarn and performance of energy harvester. A) Configuration of twistron yarn harvesters with photographic image. B) Capacitance change (black square) and open circuit voltage (blue circle) of CNT yarns that wrapped on rubber fiber clockwise direction with 70% strain. Twist insertion of CNT yarns were controlled from −2000 (counterclockwise direction) to 2000 (clockwise direction) turns m^{-1}. Negative sign of twist insertion (blue background) represent heterochiral CNT yarn, and positive sign of twist insertion (red background) represent homochiral CNT yarn. C) Capacitance (black) and peak-to-peak open circuit voltage (blue) versus strain of the homochiral (square) and heterochiral (circle) CNT yarn enwrapping rubber. D) Open circuit voltage of one-body energy harvester with sinusoidal 70% strain at 1 Hz frequency. E) Peak voltage (black square) and peak power (blue circle) versus load resistance. F) Peak power (black square) and load resistance (blue circle) for impedance matching versus frequency. B) and C) were measured by three electrochemical cell in 0.1 M HCl electrolyte (Working electrode: CNT yarn, Counter electrode: Pt/CNT buckypaper, Reference electrode: Ag/AgCl). Capacitance was measured from 0 to 0.8 V (Ag/AgCl) with scan rate of 50 mV s^{-1}. D–F) were measured by two electrochemical cell in 0.1 M HCl/PVA 10 wt% solid electrolyte (Working electrode: homochiral CNT yarn, Counter electrode: heterochiral CNT yarn).

Figure 2A shows a detailed photograph of the homochiral and heterochiral yarns wrapped around the silicone rubber fiber and schematic image of the one-body twistron yarn harvester. The red part of the photograph and red inner yarn of the schematic image show the homochiral CNT yarn, and the pink part of the photograph and pink inner yarn of the schematic image show the heterochiral CNT yarn. When wrapping the CNT yarns around the silicone rubber fiber, both yarns tend to draw near each other because of the opposite direction of the twist insertion. Thus, polyurethane was coated on both of the electrode yarns for the separator. This polyurethane coating prevents the homochiral and heterochiral yarns from contacting each other and allows the ions to pass into the CNT yarn by absorbing the solid electrolyte without a hitch (Figure S2, Supporting Information). The important thing for wearable textile applications is to transform our electrolyte-bath-operated harvester fiber into a lightweight, dual-electrode harvester yarn that operates in air. In this regard, the modified one-body twistron yarn harvester was fabricated and was composed of a solid electrolyte gel (comprising 10 wt% polyvinyl alcohol, PVA, in 0.1 M HCl), silicone rubber and a silicone tube with the polyurethane-coated homochiral and heterochiral yarns, as shown in the left configuration of Figures 1A and 2A.

To optimize the performance of these twistron yarn harvesters, the performance of the CNT yarns, that of each of the yarns wrapped on the rubber fiber, was explored using three electrochemical cells, in which the CNT yarn electrode, Pt/CNT buckypaper, and Ag/AgCl are connected to the working, counter and reference electrodes, respectively, in a 0.1 M HCl liquid electrolyte. The CNT yarns were prepared from the MWNT sheets by inserting twists from −2000 to 2000 turns m^{-1}, and the capacitance change and peak-to-peak open circuit voltage (OCV) of each CNT yarn were measured with a 70% strain, as shown in Figure 2B. As the twist insertion of the homochiral CNT yarns was increased in the clockwise direction from 0 to 2000 turns m^{-1}, the capacitance changes of the homochiral CNT yarn decreased, and their peak-to-peak OCV increased. On the other hand, as the twist insertion of the heterochiral CNT yarns was increased in the counterclockwise direction from 0 to −2000 turns m^{-1} (a negative twist insertion means that the directions of twisting and coiling the CNT yarns are opposite), the capacitance changes of the CNT yarns increased, and the peak-to-peak OCV of the CNT yarns decreased. For both the homochiral and heterochiral yarns, the twisted yarns up to just before coiling (2000 turns m^{-1} for the homochiral yarn and

–2000 turns m^{-1} for the heterochiral yarn) exhibit the best performance. In this condition, the homochiral yarn has a –31.54% capacitance change and 57.2 mV peak-to-peak OCV, and the heterochiral yarn has a 7.85% capacitance change and 9.1 mV peak-to-peak OCV at 70% strain (Figure 2B,C and Figure S3, Supporting Information).

The reason for these results can be found in the reported coiled CNT yarn twistron harvester.[25] When stretching coiled CNT yarn, the twist of the coiled CNT yarn is increased. As a result, densification occurs on a scale comparable to the electrochemical double layer thickness, and some pores in the yarn become too small to accommodate electrolyte ions; thus, the effective surface area and corresponding capacitance of the yarn decreases. Since the associated charge cannot redistribute over charged surfaces that have maintained contact with the bulk electrolyte, solvated ions migrate into the electrode's decreased accessible surface area, thus increasing the surface charge density and consequently increasing the yarn voltage. Based on this principle, Figure 1B shows a scheme of the homochiral yarn up-twist and heterochiral yarn down-twist as the twistron yarn harvester was stretched. When stretching the twistron yarn harvester, the homochiral yarn up-twist causes the yarn's density to decrease and the OCV to increase, while the heterochiral yarn down-twist causes the yarn's density to increase and the OCV to decrease. Similar principles can be found in previously reported artificial muscle based on twist carbon nanotube yarn[28] and nylon.[29]

In addition, it is possible to explain why the performance is better with more twist. When stretching 70% of the highly twisted yarn and non-twisted yarn, both enwrapping the rubber fiber in the electrolyte, the capacitance of the highly twisted yarn (2000 turns m^{-1}) has decreased by 31.54% (from 2.51 to 1.72 F g^{-1}), while the density increases from 1.00 to 1.17 g cm^{-3} (a 16.1% increase) by the up-twist, as shown in Figure S4A (Supporting Information). The non-twisted yarn's capacitance has barely changed, while the yarn's density has changed from 0.656 to 0.664 g cm^{-3} (a 1.3% change). This evidence suggests that the highly twisted yarn results in a higher generated electrical energy. However, it can be observed that the OCV of the homochiral yarn is larger than the OCV of the heterochiral yarn, as shown in Figure 2B,C. The reason is that the density changes of the homochiral and heterochiral yarn were different. When applying 70% stretching in the electrolyte, the density change of the homochiral yarn was 16.1% by the up-twist (Figure S4A, Supporting Information), while the heterochiral yarn's density decreased from 1.21 to 1.17 g cm^{-3} (–3.7% by the untwist), as shown in Figure S4B (Supporting Information).

While stretching a single harvester electrode, measuring the voltage with respect to a static counter electrode, as shown in Figure 2C, provides a good way to characterize this electrode, and the voltage and power output can be maximized by simultaneously using both the working and counter electrodes as mechanical energy harvesters. When each of the homochiral and heterochiral yarn electrodes generated 57.2 and –9.2 mV peak-to-peak OCVs with a 70% maximum strain applied, respectively (Figure 2C and Figure S3, Supporting Information), if both electrodes are used simultaneously as the working and counter electrodes, as shown in Figure 2A, this one-body twistron yarn harvester can theoretically generate the difference in the peak-to-peak OCV of the homochiral and heterochiral yarns, as shown in the blue-shaded part of Figure 2C, and experimentally generate a 67.8 mV peak-to-peak OCV at a 70% strain and 1 Hz sinusoidal stretching, as shown in Figure 2D. Compared with the calculated value of 66.4 mV, which is the difference in the peak-to-peak OCVs of the homochiral and heterochiral yarns at a 70% applied strain, the experimental result reflects a reasonable value. According to the OCV and peak power versus the spring index of the homochiral and heterochiral yarn, the lower spring index harvester generated much more energy than the higher spring index harvester (Figure S5, Supporting Information). Compared with the previously reported twistron harvesters composed of separated homochiral yarn and heterochiral yarn without Pt wire wrapping (which results in a lower impedance), which have a spring index of 4.28,[25] the OCV and total peak power of the one-body harvester without Pt wire wrapping increased by ≈1.9 times during sinusoidal stretching at 1 Hz and realizing motion (Figure S5, Supporting Information). According to a previous report about a twistron harvester,[25] the breathing sensor was shown, which consisted of separated homochiral CNT yarn and heterochiral yarn used as the working and counter electrodes, respectively. Likewise, as shown in Figure 2C,D, since the output voltage of this one-body harvester is dependent on the strain, this stretchable twistron yarn harvester can be a self-powered strain sensor. Figures S6 and S7 (Supporting Information) showed the mechanical and long-term stability by stretching up to 1200 cycles and the fibrous mechanical properties by stress–strain curve of the yarn harvester.

A maximum peak power generated at 1 Hz was obtained by impedance matching the twistron yarn harvester, as shown in Figure 2E. The generated voltage increased with increasing the load resistance, but the peak power of the twistron yarn harvester was saturated at a load resistance of 100 Ω. Thus, at 1 Hz of stretching, a peak power of 2.7 W kg^{-1} was generated. The impedance of the twistron yarn harvester is related to the reactance of the EDL capacitance of the electrodes. This capacitive reactance is inversely proportion to the frequency of the AC current of the electrodes, and therefore, when increasing the frequency of stretching, the impedance of the harvester decreases.[25] In this sense, Figure 2F shows that the load resistance decreased from 170 to 40 Ω, which was obtained by impedance matching the twistron yarn harvester, and the generated peak power increased from 1.5 to 5.3 W kg^{-1} as the frequency was increased from 0.5 to 4 Hz. This work can be efficiently applied to textile applications with smaller volumes, and combining two yarns together can generate more energy than the energy generated in previous twistron research.

Additionally, as abovementioned, twistron yarn harvesters can be used as elastic yarn supercapacitors by controlling the twist insertion of the CNT yarns. The elastic yarn supercapacitors were composed of a solid electrolyte gel (0.1 M HCl with polyvinyl alcohol and 10 wt% solid electrolyte), non-twisted yarns coated with polyurethanes used for the anode and cathode, a silicone rubber fiber and a silicone tube, as shown in Figure 1A. Unlike twistron yarn harvesters, which generate electrical energy from mechanical deformations, elastic yarn supercapacitors can store electrical energy stably for wearable applications, regardless of mechanical deformations. As shown in Figure 2B, the non-twisted yarns that had 0 turns m^{-1} of twist insertion and were wrapped around a rubber fiber featured a slight capacitance change and had little or no peak-to-peak OCV with 70% sinusoidal stretching. Thus, both the non-twisted yarns were used to prepare the anode and cathode of the elastic yarn supercapacitor.

2.2. The Solid-State Yarn Supercapacitor

Figure 3 showed the electrochemical energy storage performance of the elastic yarn supercapacitors in a solid electrolyte gel (10 wt% PVA/0.1 M HCl). The cyclic voltammetry (CV) curves were obtained by various scan rates from 100 to 1000 mV s^{-1}, and Galvanostatic charge–discharge curves were obtained for various current densities from 0.11 to 0.55 A g^{-1} (Figure 3A,B). The elastic yarn supercapacitor had a capacitance of 1.49 F g^{-1}, 0.7 mF cm^{-1} and 17.0 mF cm^{-2} at a scan rate of 100 mV s^{-1} and a capacitance retention of 65.8% with various scan rates (Figure 3C). At a scan rate of 50 mV s^{-1}, the elastic yarn supercapacitor not only provided a constant capacitance from 1.54 to 1.5 F g^{-1} (capacitance change <3%) for a strain of 0% to 70% (Figure 3D) but also exhibited a stable electrochemical storage capacity with dynamic sinusoidal stretching of 70% and 180° bending deformation applied during 1000 cycles, as shown in Figure 3E,F. This means that this elastic yarn supercapacitor can be a highly stable energy storage system when used for applications with dynamic conditions. Since our yarn harvester and supercapacitor are packed by silicone rubber tube, the electrolyte and electrodes are sealed tightly from outer environment. In this reason, it assumes to be used semi-permanently without damage of silicone rubber tube.

Since human motion generally has a frequency between 0 and 10 Hz,[30] these dynamic results are important for wearable devices. When increasing the frequency of stretching and releasing at 1 Hz, the elastic yarn supercapacitor exhibits stable charging and discharging CV curves with slight fluctuations compared to the CV curve obtained without 70% stretching (inset of Figure 3E). In addition, it is important to configure the anode and cathode of the supercapacitor to prevent the short problem. Several supercapacitor fibers made using a two-ply or parallel configuration of the anode and cathode have short problem when a mechanical deformation or pressure is app lied.[5,7,11–12,14,16–18] In this regard, the configuration of the elastic

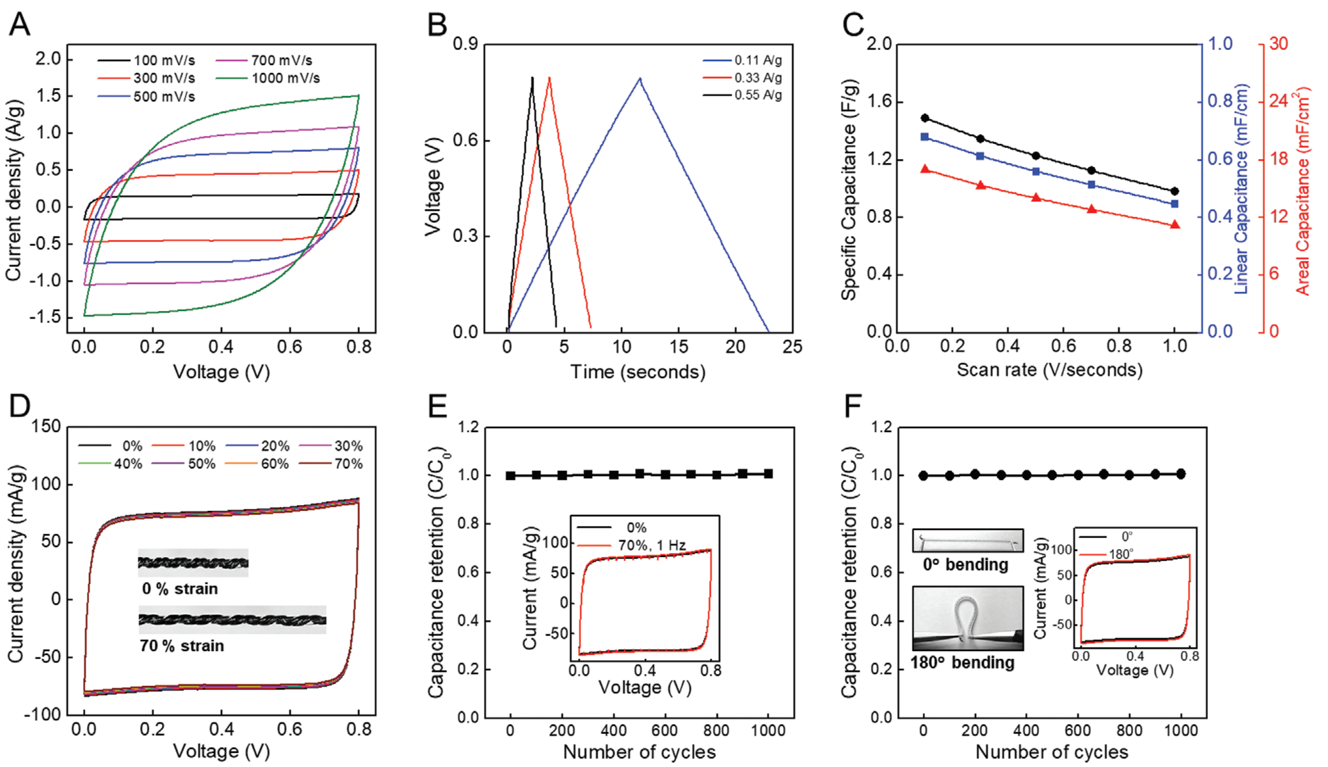

Figure 3. Electrochemical performance of the solid-state elastic yarn supercapacitor. A) Cyclic voltammetry (CV) curves measured from 100 to 1000 mV s^{-1} for a solid-state elastic yarn supercapacitor coated by solid electrolyte gel (comprising 10 wt% polyvinyl alcohol, PVA, in 0.1 M HCl). B) Galvanostatic charge/discharge curves measured from 0.11 to 0.55 A g^{-1} current densities. C) Calculated specific capacitance (normalized by anode and cathode weight, black circle symbols), linear capacitance (normalized by length of supercapacitor, blue rectangular symbols), and areal capacitance (normalized by the surface area of supercapacitor, red triangle symbols) at scan rate from 100 to 1000 mV s^{-1}, respectively. D) Static CV curve of the solid-state elastic yarn supercapacitors for 0–70% tensile strain. E) and F) showed capacitance retention during 1000 cycles mechanical deformation with sinusoidal stretching and 180° bending motion, respectively. Capacitance of E) and F) was measured after mechanical deformation. Inset of D) showed optical images of before and after of stretching 70%. Inset of E) showed dynamic CV curve of the solid-state elastic yarn supercapacitors with non-stretching (black line) and 1 Hz stretching 70% strain (red line). Inset of F) showed optical images of before and after of bending 180° and CV curve of the solid-state elastic yarn supercapacitors with non-bending (black line) and 180° bending state (red line). CV curve of D–F) was measured with potential scan rate of 50 mV s^{-1}.

yarn supercapacitors has advantage of preventing shorts from occurring between the anode and cathode under mechanical deformation, because both yarns were helically wound in parallel on the rubber and coated with polyurethane.

2.3. Energy Generating and Storing Textile

We demonstrated an energy generating and storing textile using optimized twistron yarn harvesters (Figure 2) and elastic yarn supercapacitors (Figure 3). The twistron yarn harvesters and elastic yarn supercapacitors cross each other (in the vertical direction of each other) and were made up of a plain weave, as shown in **Figure 4**A. To increase the voltage generated in the package, the twistron yarn harvesters are connected in series, while the elastic yarn supercapacitors are connected in parallel to increase the amount of Q stored. Figure 4B showed a real image of a wearable patch (whose harvesting and storing area size has a width of 3 and height of 3 cm) on a human knee, and the patch had 9-twistron yarn harvesters in the longitudinal direction and the 3-elastic yarn supercapacitors in the transverse direction. When connecting up to 9 in series, the voltage increases in proportion to the number of twistron yarn harvesters, up to 550 mV for 70% stretching (Figure 4C).

Since twistron yarn harvesters produce an AC voltage, a rectification process using a bridge rectifier is required to store electrical energy in the elastic yarn supercapacitors. Figure S8 (Supporting Information) showed charging and discharging process of yarn supercapacitor by schematic image. Figure 4D showed the OCV and rectified voltage obtained from 9-twistron yarn harvesters connected in series. The peak rectified voltage was 135 mV, which was less than the peak generated voltage due to the voltage drop across the Schottky diode rectifier. Figure 4E showed the charging and discharging of the elastic yarn supercapacitors by twistron yarn harvesters. By one stretching of the twistron yarn harvesters which 5.8 N of strain force was applied for 9 harvesters, the voltage on the elastic yarn supercapacitors (6.15 mF) reached ≈48 mV. Thus, when stretching the twistron yarn harvesters three consecutive times, the elastic yarn supercapacitors are fully charged at ≈135 mV.

The power consumption from 10 to 100 µW generally can utilize for RFID tag, hearing aid, and remote control.[31] In our device, the charged voltage and capacitance of parallel connected supercapacitors was about 135 mV, 6.15 mF, respectively. So, the output energy was about 56 µJ from the equation $E = 0.5CV^2$. This result assumes that our device can supply abovementioned power consumption when charged a few seconds.

To improve the performances of generating an electrical voltage from this textile, just increasing the number of twistron

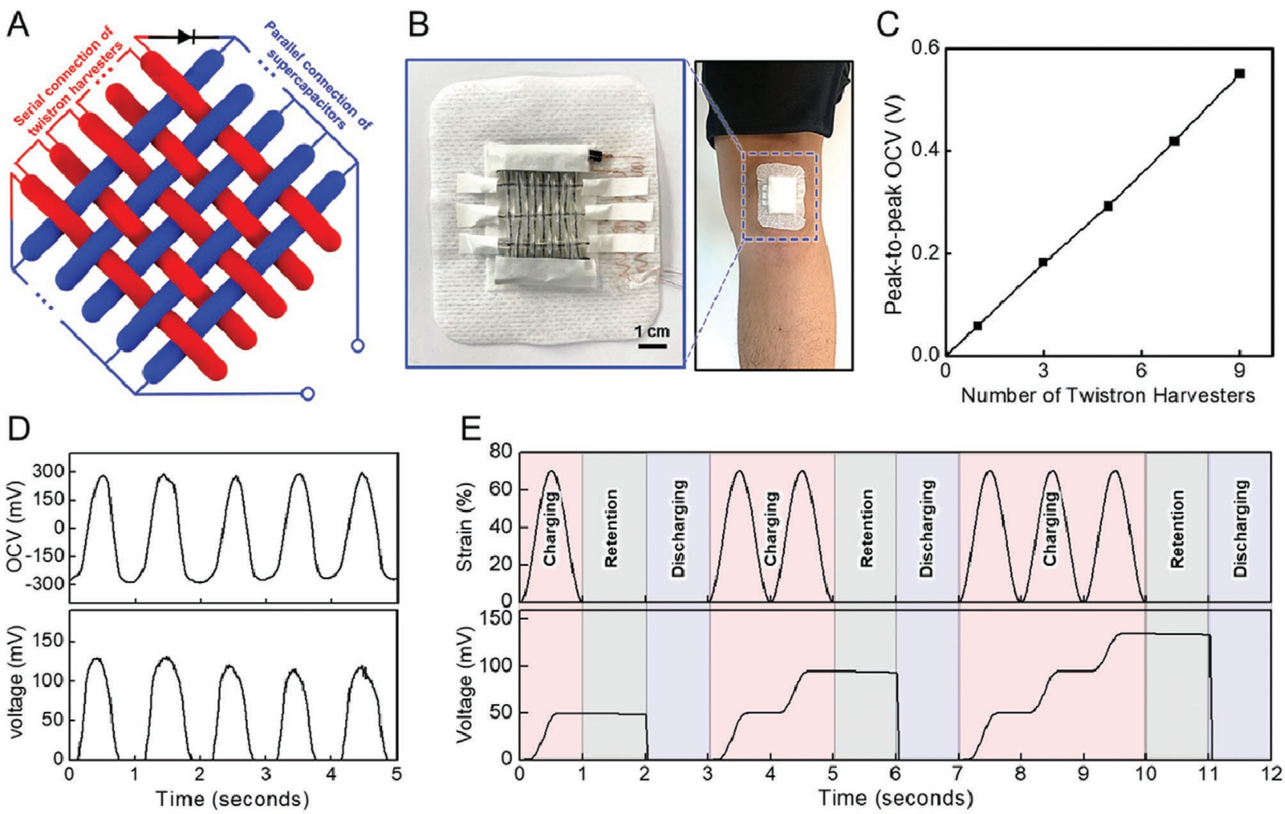

Figure 4. Scale up and charging performance using energy generating and storing textile. A) Schematic image of electrical circuit of energy generating and storing textile. Red represent energy harvester and blue represent supercapacitor. Energy harvester has serial connection, and supercapacitor has parallel connection. B) Optical images of real application of energy generating and storing textile using stretchable medical patch on human skin. C) OCV versus number of twistron yarn harvesters. D) OCV and rectified OCV at 1 Hz from rectification circuit. E) The time dependence of elastic yarn supercapacitors voltage when charging parallel connected three of elastic yarn supercapacitors.

yarn harvesters is the easy way. Although our study demonstrated that the voltage may be impractical due to its small size, increasing the number of twistron yarn harvesters to 20 can produce a rectified voltage of 1 V, as expected. Additionally, there are many reports about high performance supercapacitors based on CNTs. Since the elastic yarn supercapacitor's energy storing performance originates from the CNTs, the energy storage performance of this elastic yarn supercapacitor can be improved by various methods, such as simply connecting a few more yarn supercapacitors in series or in parallel, biscrolling, or coating with pseudocapacitance materials.[5,16,18]

3. Conclusion

We have reported highly stretchable yarn type energy harvester and supercapacitor which mechanism and performances based on twist insertion of CNT yarns. Unlike triboelectric or piezoelectric harvesters and other fiber type supercapacitor, our twistron yarn harvesters and elastic yarn supercapacitor with unique design can produce electrical energy and store it stably at the same time from mechanical deformation with low frequency of human body movements. Since our generator and storage integral textile that based on silicone rubber fibers and CNT yarns is highly flexible and stretchable, it is greatly suitable form for applying wearable materials, such as cloth, patch, or band.

Also, we expect fresh applications for soft robotics. Currently, many of soft robots are consisted of stretchable materials, such as silicone or urethane rubber. Since silicone rubber fiber was used for core stretchable fiber of both of harvester and supercapacitor, lower tensile strength was applied unlike previous coiled CNT yarn harvesters. Therefore, if core rubber fiber replaced to soft robots based on stretchable rubber materials, soft robots that generate energy and store it by itself can be produced.

Furthermore, any number of harvesters and supercapacitors can be connected by series or parallel each other for scale-up of generating and storing electrical energy. This expendable performance can be applied for powering wearable devices and activating sensors. Even this strain reliant energy harvester can be a strain sensor by itself.

4. Experimental Section

Materials: MWNT forests were grown by chemical vapor deposition (CVD) on silicon wafers that were coated by a 3-nm-thick iron catalyst.[27] Silicone rubber, which was purchased from Hyup-shin Corporation in Korea, was made by Smooth-on, Inc. in the USA. The silicone rubber fiber was synthesized by mixing "Echoflex 0050" and "Dragon skin 10" with a mix ratio of 3:1 by weight and then injecting and hardening in injection needles with a 0.5 mm inner diameter. After that, the hardened silicone rubber fiber was pulled out. The rubber tube (inner diameter: 0.5 mm, outer diameter: 1 mm) was purchased from HSW, Inc. in Korea. The solid electrolyte gel (comprising 10 wt% polyvinyl alcohol, PVA, in 0.1 м HCl) was made by stirring on a hot plate at 90 °C. PVA (Mw: 31 000–50 000) and HCl (37%) were purchased from Sigma Aldrich. Both the twistron fiber harvester and supercapacitor were explored by twist inserting into a carbon nanotube sheet. The twisting structure of the yarns was a cone structure, which was uniformly stressed during twisting.[25 The twist insertion into the CNT yarn was typically accomplished by hanging a weight from one end of a fiber and attaching the other end to the shaft of a motor. The attached weight was tethered against the rotation so that each turn of the motor resulted in the addition of one turn to the fiber. The applied weight was critical in maintaining a uniform fiber density after just enough twist was inserted before coiling. The CNT yarns were twisted at loads of 33.5 MPa.

Fabrication of Twistron Yarn Harvesters and Elastic Yarn Supercapacitors: The twistron yarn harvesters were fabricated from highly twisted yarns with the coiling of silicone rubber. First, a MWNT yarn twisted in a clockwise direction and a MWNT yarn twisted in a counterclockwise direction were prepared by high twist insertion into MWNT sheets under an isobaric load before coiling. Second, to prevent the short-circuit problem, both of the yarns were coated with polyurethane (10 wt%). Then, both the polyurethane-coated yarns were wound around a 250 μm diameter rubber mandrel (diameter before stretch was 500 μm), which was stretched by 300, in the same clockwise direction using two stepping motors (A16K-M569, Autonics, Corp.) with a turning speed of 1 turns s^{-1} (Figure S1A, Supporting Information). Finally, the homochiral and heterochiral yarns wrapped on the rubber fiber were inserted in a rubber tube, which had an ≈1 mm inner diameter and 2 mm outer diameter. After that, the solid electrolyte (10 wt% PVA in 0.1 м HCl) was injected using a syringe. Additionally, the elastic yarn supercapacitor was composed of two non-twisted yarns coated with polyurethane. The processes of fabricating the elastic yarn supercapacitors were the same as those used to fabricate the twistron yarn harvesters, but the only difference was the twist insertion and direction of the CNT yarns. Unlike the twistron yarn harvesters that generated electrical energy with mechanical deformations, the elastic yarn supercapacitors should be able to store electrical energy stably for wearable applications, regardless of mechanical deformations.

Electrochemical Methods for Characterizing: The experiments were conducted by a three-electrode system, in which the working electrode was the CNT yarns, the counter electrode was Pt mesh/CNT buckypaper, and the reference electrode was Ag/AgCl. To measure the OCV, short-circuit current, and capacitance, three different techniques were applied using of a Gamry instrument (model G750), and repeating chronopotentiometry, repeating chronoamperometry mode, and CV were used.

Power Measurement and Calculation: To measure the electrical power and electrical energy, the twistron harvester was connected to an external resistance. By changing the external resistance, the applied voltage on the external resistance was measured by an oscilloscope (Tektronix, DPO4014B). With the acquired results from the oscilloscope, the electrical power ($P = V^2/R$, where P = power, V = voltage, and R = resistance) and electrical energy ($\int P/t$, where P = power and t = time) were measured.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the Creative Research Initiative Center for Self-Powered Actuation of the National Research Foundation and the Ministry of Science and ICT (MSIT) in Korea. This work was also supported in in the USA by Air Force Office of Scientific Research grants FA9550-15-1-0089 and FA9550-12-1-0035, Air Force Grant AOARD-FA2386-13-4119, NASA project NNX15CS05C, Robert A. Welch Foundation grant AT-0029, and Office of Naval Research grant N00014-14-1-0158. Informed consent was obtained from the volunteer (T.J.M.) for the tests performed with the developed textile on their skin.

Conflict of Interest

The authors declare no conflict of interest.

Author Contribution

T.J.M., S.H.K., and S.J.K. conceived the idea. T.J.M., J.W.P., and J.H.M. performed the experiments. T.J.M. and J.W.P. graphed and analyzed the data. C.H. manufactured and supplied experiment materials (carbon nanotubes forest). T.J.M., Y.J., R.H.B., and S.J.K. wrote the paper. All authors discussed the results and commented on the manuscript.

Keywords

carbon nanotube yarn, energy harvester, intelligent textile, stretchable strain senor, supercapacitor

Received: January 15, 2020
Revised: February 24, 2020
Published online: April 13, 2020

[1] X. Pu, L. Li, M. Liu, C. Jiang, C. Du, Z. Zhao, W. Hu, Z. L. Wang, *Adv. Mater.* **2016**, *28*, 98.
[2] J. Liang, G. Zhu, C. Wang, Y. Wang, H. Zhu, Y. Hu, H. Lv, R. Chen, L. Ma, T. Chen, Z. Jin, J. Liu, *Adv. Energy Mater.* **2017**, *7*, 1601208.
[3] J. Bae, Y. J. Park, M. Lee, S. N. Cha, Y. J. Choi, C. S. Lee, J. M. Kim, Z. L. Wang, *Adv. Mater.* **2011**, *23*, 3446.
[4] X. Pu, L. Li, H. Song, C. Du, Z. Zhao, C. Jiang, G. Cao, W. Hu, Z. L. Wang, *Adv. Mater.* **2015**, *27*, 2472.
[5] C. Choi, J. A. Lee, A. Y. Choi, Y. T. Kim, X. Lepró, M. D. Lima, R. H. Baughman, S. J. Kim, *Adv. Mater.* **2014**, *26*, 2059.
[6] J. A. Lee, M. K. Shin, S. H. Kim, H. U. Cho, G. M. Spinks, G. G. Wallace, M. D. Lima, X. Lepro, M. E. Kozlov, R. H. Baughman, S. J. Kim, *Nat. Commun.* **2013**, *4*, 1970.
[7] D. Zhang, M. Miao, H. Niu, Z. Wei, *ACS Nano* **2014**, *8*, 4571.
[8] X. Chen, H. Lin, J. Deng, Y. Zhang, X. Sun, P. Chen, X. Fang, Z. Zhang, G. Guan, H. Peng, *Adv. Mater.* **2014**, *26*, 8126.
[9] H. Sun, X. You, J. Deng, X. Chen, Z. Yang, J. Ren, H. Peng, *Adv. Mater.* **2014**, *26*, 2868.
[10] Z. Yin, X. Zhang, Y. Cai, J. Chen, J. I. Wong, Y. Y. Tay, J. Chai, J. Wu, Z. Zeng, B. Zheng, H. Y. Yang, H. Zhang, *Angew. Chem., Int. Ed. Engl.* **2014**, *53*, 12560.
[11] W. Weng, Q. Sun, Y. Zhang, H. J. Lin, J. Ren, X. Lu, M. Wang, H. S. Peng, *Nano Lett.* **2014**, *14*, 3432.
[12] Q. H. Meng, K. Wang, W. Guo, J. Fang, Z. X. Wei, X. L. She, *Small* **2014**, *10*, 3187.
[13] Y. Huang, H. Hu, Y. Huang, M. S. Zhu, W. J. Meng, C. Liu, Z. X. Pei, C. L. Hao, Z. K. Wang, C. Y. Zhi, *ACS Nano* **2015**, *9*, 4766.
[14] L. B. Liu, Y. Yu, C. Yan, K. Li, Z. J. Zheng, *Nat. Commun.* **2015**, *6*, 3187.
[15] H. Sun, X. M. Fu, S. L. Xie, Y. S. Jiang, H. S. Peng, *Adv. Mater.* **2016**, *28*, 2070.
[16] C. Choi, H. J. Sim, G. M. Spinks, X. Lepro, R. H. Baughman, S. J. Kim, *Adv. Energy Mater.* **2016**, *6*, 1502119.
[17] Z. T. Zhang, J. Deng, X. Y. Li, Z. B. Yang, S. S. He, X. L. Chen, G. Z. Guan, J. Ren, H. S. Peng, *Adv. Mater.* **2015**, *27*, 356.
[18] C. Choi, S. H. Kim, H. J. Sim, J. A. Lee, A. Y. Choi, Y. T. Kim, X. Lepro, G. M. Spinks, R. H. Baughman, S. J. Kim, *Sci. Rep.* **2015**, *5*, 9387.
[19] S. Lee, W. Ko, Y. Oh, J. Lee, G. Baek, Y. Lee, J. Sohn, S. Cha, J. Kim, J. Park, J. Hong, *Nano Energy* **2015**, *12*, 410.
[20] P. K. Yang, L. Lin, F. Yi, X. H. Li, K. C. Pradel, Y. L. Zi, C. I. Wu, J. H. He, Y. Zhang, Z. L. Wang, *Adv. Mater.* **2015**, *27*, 3817.
[21] F. Yi, X. F. Wang, S. M. Niu, S. M. Li, Y. J. Yin, K. R. Dai, G. J. Zhang, L. Lin, Z. Wen, H. Y. Guo, J. Wang, M. H. Yeh, Y. L. Zi, Q. L. Liao, Z. You, Y. Zhang, Z. L. Wang, *Sci. Adv.* **2016**, *2*, e1501624
[22] H. J. Sim, C. Choi, S. H. Kim, K. M. Kim, C. J. Lee, Y. T. Kim, X. Lepro, R. H. Baughman, S. J. Kim, *Sci. Rep.* **2016**, *6*, 35153.
[23] H. J. Sim, C. Choi, C. J. Lee, Y. T. Kim, S. J. Kim, *Curr. Nanosci.* **2015**, *11*, 539.
[24] X. H. Li, Z. H. Lin, G. Cheng, X. N. Wen, Y. Liu, S. M. Niu, Z. L. Wang, *ACS Nano* **2014**, *8*, 10674.
[25] S. H. Kim, C. S. Haines, N. Li, K. J. Kim, T. J. Mun, C. Choi, J. T. Di, Y. J. Oh, J. P. Oviedo, J. Bykova, S. L. Fang, N. Jiang, Z. F. Liu, R. Wang, P. Kumar, R. Qiao, S. Priya, K. Cho, M. Kim, M. S. Lucas, L. F. Drummy, B. Maruyama, D. Y. Lee, X. Lepro, E. L. Gao, D. Albarq, R. Ovalle-Robles, S. J. Kim, R. H. Baughman, *Science* **2017**, *357*, 773.
[26] Y. Jang, S. M. Kim, G. M. Spinks, S. J. Kim, *Adv. Mater.* **2019**, 1902670.
[27] M. Zhang, S. L. Fang, A. A. Zakhidov, S. B. Lee, A. E. Aliev, C. D. Williams, K. R. Atkinson, R. H. Baughman, *Science* **2005**, *309*, 1215.
[28] M. D. Lima, N. Li, M. J. de Andrade, S. L. Fang, J. Oh, G. M. Spinks, M. E. Kozlov, C. S. Haines, D. Suh, J. Foroughi, S. J. Kim, Y. S. Chen, T. Ware, M. K. Shin, L. D. Machado, A. F. Fonseca, J. D. W. Madden, W. E. Voit, D. S. Galvao, R. H. Baughman, *Science* **2012**, *338*, 928.
[29] C. S. Haines, M. D. Lima, N. Li, G. M. Spinks, J. Foroughi, J. D. W. Madden, S. H. Kim, S. L. Fang, M. J. de Andrade, F. Goktepe, O. Goktepe, S. M. Mirvakili, S. Naficy, X. Lepro, J. Y. Oh, M. E. Kozlov, S. J. Kim, X. R. Xu, B. J. Swedlove, G. G. Wallace, R. H. Baughman, *Science* **2014**, *343*, 868.
[30] J. Lester, B. Hannaford, G. Borriello, presented at *Int. Conf. Pervasive Comput.*, Berlin, Heidelberg April **2004**.
[31] R. Arai, S. Furukawa, N. Sato, T. Yasuda, *J. Mater. Chem. A* **2019**, *7*, 20187.