AFRL-AFOSR-VA-TR-2018-0342

Twist-Spun Polymer and Nanotube Artificial Muscle Fibers and Yarns Powered Thermally, Chemically, and Electrochemically

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07/17/2018
Final Report

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Arlington, Virginia 22203
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REPORT DOCUMENTATION PAGE

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1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
13/07/2018	Final	15/04/2015-14/04/2018

4. TITLE AND SUBTITLE
Twist-Spun Polymer and Nanotube Artificial Muscle Fibers and Yarns Powered Thermally, Chemically, and Electrochemically

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA9550-15-1-0089

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Baughman, Ray

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
THE UNIVERSITY OF TEXAS AT DALLAS
800 W CAMPBELL RD
RICHARDSON TX 75080-1407

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

13. SUPPLEMENTARY NOTES

14. ABSTRACT

We have published 32 project-supported archival publications during this three-year project, many of which have been in high impact journals (including 2 in Science and 7 in the Nature family of journals). Five of these articles have been featured as journal covers. Also, we have filed PCT/US utility patents on four different project-supported inventions. Between 2016 and 2018, 12 US patents (and many more foreign patents) were issued for our AFOSR-supported inventions. This final report provides a brief summary of all work, and more complete description of recent work. This description will focus on our artificial muscles run-in-reverse to harvest mechanical energy as electrical energy (twistrons), which were not previously described in any enabling detail in our first two annual reports, since they are publicly available documents and patent filings had not yet been made.

15. SUBJECT TERMS
Carbon nanotubes, artificial muscles, energy harvesting, twistron

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE	SAR	14	Dr. Steve Collins
					19b. TELEPHONE NUMBER *(Include area code)* 972-883-6534

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Final Report for FA9550-15-1-0089 on "Twist-Spun Polymer and Nanotube Artificial Muscle Fibers and Yarns Powered Thermally, Chemically, and Electrochemically"

Abstract: We have published 32 project-supported archival publications during this three-year project, many of which have been in high impact journals (including 2 in *Science* and 7 in the *Nature* family of journals). Five of these articles have been featured as journal covers. Also, we have filed PCT/US utility patents on four different project-supported inventions. Between 2016 and 2018, 12 US patents (and many more foreign patents) were issued for our AFOSR-supported inventions. This final report provides a brief summary of all work, and more complete description of recent work. This description will focus on our artificial muscles run-in-reverse to harvest mechanical energy as electrical energy (twistrons), which were not previously described in any enabling detail in our first two annual reports, since they are publically available documents and patent filings had not yet been made. Project advances during this three year period have included: (A) Hierarchically buckled sheath-core fibers for superelastic electronics, sensors, and muscles; (B) Polymer muscles that harvest the energy of temperature fluctuations as electrical energy; (C) High performance electrochemical and electrothermal artificial muscles from twist-spun carbon nanotube yarn; (D) A self-powered enzyme-based thermal carbon nanotube muscle that provides reversible torsional actuation in response to changes in glucose concentration; (E) A self-powered glucose-driven artificial muscle that uses swelling/un-swelling caused by the reversible binding of glucose to boronic acid; (F) An incandescent tensile anneal process (ITAP) that increases muscle strength and avoids the need for torsional tethering; (G) A first large-stroke, high-contractile-energy carbon nanotube electrochemical muscle; (H) A magnetically actuated carbon-nanotube yarn muscle; (I) Harvesting electrical energy from torsional thermal actuation driven by natural convection; and (J) Artificial muscles that are driven in reverse to generate electrical energy.

1. OVERVIEW OF PROJECT RESULTS

(A) *Hierarchically buckled sheath-core fibers for superelastic electronics, sensors, and muscles* (*Science* **349**, 400-404 (2015)): We reported the fabrication of highly stretchable (up to 1320%) sheath-core conducting fibers created by wrapping carbon nanotube sheets oriented in the fiber direction on stretched rubber fiber cores. The resulting structure exhibited distinct short- and long-period sheath buckling that occurred reversibly out-of-phase in the axial and belt directions, enabling a resistance change of less than 5% for a 1000% stretch. By including other rubber and carbon nanotube sheath layers, we demonstrated strain sensors generating an 860% capacitance change and electrically powered torsional muscles operating reversibly by a coupled tension-to-torsion actuation mechanism. Using theory, we quantitatively explain the complementary effects of an

increase in muscle length and a large positive Poisson's ratio on torsional actuation and electronic properties.

(B) *Harvesting temperature fluctuations as electrical energy using torsional and tensile polymer muscles* (*Energy & Environmental Science* **8**, 3336-3344 (2015)): We reported the electromagnetic harvesting of thermal energy as electrical energy using thermally powered torsional and tensile artificial muscles made from inexpensive polymer fibers used for fishing line and sewing thread. We show that a coiled 27 mm-diameter nylon muscle fiber can be driven by 16.7 °C air temperature fluctuations to spin a magnetic rotor to a peak torsional rotation speed of 70,000 rpm for over 300,000 heating–cooling cycles without performance degradation. By employing resonant fluctuations in air temperature of 19.6 °C, an average output electrical power of 124 W per kg of muscle was realized. Using tensile actuation of polyethylene-based coiled muscles and alternating flows of hot and cold water, up to 1.4 J of electrical energy was produced per cycle. The corresponding per cycle electric energy and peak power output, per muscle weight, were 77 J/kg and 28 W/kg, respectively.

(C) *High performance electrochemical and electrothermal artificial muscles from twist-spun carbon nanotube yarn* (*Nano Convergence* 2015, 2:8 doi:10.1186/s40580-014-0036-0): High performance torsional and tensile artificial muscles were obtained, which utilize thermally- or electrochemically-induced volume changes of twist-spun, guest-filled, carbon nanotube (CNT) yarns. These yarns were prepared by incorporating twist in carbon nanotube sheets drawn from spinnable CNT forests. Inserting high twist into the CNT yarn results in yarn coiling, which can dramatically amplify tensile stroke and work capabilities compared with that for the non-coiled twisted yarn. When electrochemically driven in a liquid electrolyte, these artificial muscles can generate a torsional rotation per muscle length that is over 1000 times higher than for previously reported torsional muscles. All-solid-state torsional electrochemical yarn muscles have provided a large torsional muscle stroke (53° per mm of muscle length) and a tensile stroke of up to 1.3% when lifting loads that are ~25 times heavier than can be lifted by the same diameter human skeletal muscle. Over a million torsional and tensile actuation cycles were demonstrated for thermally powered CNT hybrid yarns muscles filled with paraffin wax, wherein a muscle spins a rotor at an average 11,500 revolutions/minute or delivers 3% tensile contraction at 1200 cycles/minute. At lower actuation rates, these thermally powered muscles provided tensile strokes of over 10%.

(D) *Biothermal sensing of a torsional artificial muscle* (*Nanoscale* **8**, 3248-3253 (2016): A self-powered actuating torsional glucose sensor was demonstrated, which utilized a biscrolled twist-spun carbon nanotube yarn in which the biscrolled yarn guest is glucose oxidase that is trapped a thermally responsive hydrogel (poly(N-isopropylacrylamide)). The heat generated, by glucose-oxidase-catalyzed oxidation of glucose, causes the thermally responsive hydrogel to expand by absorbing water, which drives the torsional actuation of the yarn muscle. The torsional actuator stroke was monotonically correlated

with glucose concentration between 5 mM and 100 mM glucose aqueous solutions and the maximum observed torsional stroke was 75° per cm of biscrolled muscle length. By replacing the glucose oxidase with another enzyme, this actuation method might be deployable for realizing actuation that opens or closes a valve in response to a biochemical, to potentially control the release of a drug.

(E) *Carbon nanotube yarn-based glucose sensing artificial muscle* (*Small* **12**, 2085-2091 (2016)): This self-powered muscle autonomously senses and correspondingly actuates by using a non-thermal mechanism. The guest within a twisted carbon nanotube yarn is a boronic acid-conjugated hyaluronic acid/cholesterol nanogel that reversibly couples with glucose, via the reversible binding properties of the boronic acid substituent, to provide actuation. This torsional actuation is driven by yarn swelling, resulting from water sorption, when non-ionic boronic-acid-derived polymer substituents become negatively charged by coupling with the glucose (thereby interrupting inter-chain bonding). The torsional actuation of the hybrid carbon nanotube muscle linearly increases with glucose concentration in the 5 mM to 20 mM range, and reaches 20° per cm of actuating muscle length.

(F) *Strong, twist-stable carbon nanotube yarns and muscles by tension annealing at extreme temperatures* (*Advanced Materials* **28**, 6598–6605 (2016)): We here provide an incandescent tension annealing process (ITAP) for stabilizing both twisted and coiled CNT yarns with respect to unwanted irreversible untwist, thereby avoiding the need to tether torsional artificial muscles, and increasing the mechanical loads that can be driven by these muscles. This ITAP involves thermally annealing twisted CNT yarns at a temperature of about 2000 °C while these yarns are under tensile loads. Depending upon the density of the precursor yarn, the ITAP increased yarn modulus and yarn strength by factors of up to 12 and 2.6, respectively. While a non-tethered pristine yarn immediately underwent irreversible untwist when strained by a freely rotating weight, a non-tethered ITAP yarn could be reversibly actuated by cyclic vapor sorption/desorption to rotate a 6100 times heavier rotor by 52° per millimeter of muscle length, thereby achieving a peak rotation speed of 160 rpm. In addition, the ITAP conferred remarkable long-term resistance to chlorosulfonic acid whose strong protonation ability caused pristine yarns to swell, disorder, and mechanically fail within minutes.

(G) *Electrochemically powered, energy-conserving carbon nanotube artificial muscles* (*Advanced Materials* **29**, 1700870 (2017)): This work demonstrates electrochemically powered carbon nanotube yarn muscles that provide tensile contraction as high as 16.5%, which is 12.7 times higher than previously obtained. These electrochemical muscles can deliver a contractile energy conversion efficiency of 5.4%, which is 4.1 times that reported for any organic-material-based artificial muscle. All-solid-state parallel muscles and braided muscles, which do not require a liquid electrolyte, provide tensile contractions of 11.6% and 5%, respectively.

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(H) *Magnetic torsional actuation of a carbon nanotube yarn artificial muscle* (*Royal Society of Chemistry Advances* **8**, 17421 (2018)): Magnetically driven torsional actuation of a multiwalled carbon nanotube (MWNT) yarn was realized by first biscrolling NdFeB magnetic particles into helical yarn corridors to make a magnetic MWNT yarn. The actuating device comprised a pristine MWNT yarn that was connected to the magnetic MWNT yarn, with a paddle attached between these yarns. The application of a magnetic field reversibly drove torsional actuation of up to 80° within ~0.67 seconds. This magnetic actuator was remotely powered, and its actuation stroke was the same when the muscle array was at 20 °C and at -100 °C.

(I) *Harvesting electrical energy from torsional thermal actuation driven by natural convection* (*Scientific Reports*, | *(2018) 8:8712* | DOI:10.1038/s41598-018-26983-4 (2018)): We have demonstrated a thermal energy harvester that is driven by the small temperature fluctuations provided by natural convection. This harvester uses coiled yarn artificial muscles, comprising well-aligned shape memory polyurethane (SMPU) microfibers, to convert thermal energy to torsional mechanical energy, which is then electromagnetically converted to electrical energy. Temperature fluctuations in a yarn muscle, having a maximum hot-to-cold temperature difference of about 13°C, were used to spin a magnetic rotor to a peak torsional rotation speed of 3,000 rpm. The electromagnetic energy generator converted the torsional energy to electrical energy, thereby producing an oscillating output voltage of up to 0.81 V and peak power of 4 W/kg, based on SMPU mass.

2. FOCUSED DESCRIPTION OF ELECTROCHEMICAL ARTIFICAL MUSCLES DRIVEN IN REVERSE TO GENERATE ELECTRICAL FROM INPUT MECHANICAL ENERGY

We long tried to operate our electrochemical artificial muscles in reverse to generate electrical energy, but were largely unsuccessful for reasons that we now understand. We did make a carbon-nanotube-based mechanical energy harvester that electrochemically generated electrical energy when a twist-spun carbon nanotube (CNT) yarn electrode was stretched, but obtained such small voltage changes and short circuit currents, even when a bias voltage was used for charge injection, that the only possible application was as a strain sensor (*1*). In contrast with this result, we are now able to generate a peak electrical power output of up to 250 W per kg of stretched yarn for our twistron energy harvester *without applying an external bias voltage*. This advance resulted in part from our transitioning from carbon nanotube yarns that are twisted, but not coiled (called twisted yarns), to yarns that are so highly twisted that they are completely coiled (called coiled yarns) for tensile mechanical energy harvesting, and by harvesting torsional mechanical energy by twist insertion into non-coiled yarns. These carbon nanotube harvesters were produced by spinning sheets of aligned carbon multi-walled nanotubes (MWNTs) into high strength yarns (*2*). These sheets are drawn from vertical forests of MWNTs produced by chemical vapor deposition (*3*). Due to their lightweight and large

internal surface area, such MWNT yarns exhibit specific capacitances of up to 15 F/g in aqueous electrolytes (*4*). By inserting extreme amounts of twist into mechanically loaded carbon nanotube yarns, the twisted yarn spontaneously forms coils, resulting in a stretchable spring-like structure.

We have two main types of twistron mechanical energy harvesters: (1) torsional mechanical energy harvesters based on CNT yarns that are twisted, but not coiled, which we name “twisted twistron harvesters” and (2) tensile mechanical energy harvesters that are fully coiled by twist insertion, which we name “coiled twistron harvesters”. We call these devices twistron harvesters (using “tron” from the Greek suffix, meaning device), since we have discovered that these electrochemical harvesters operate by using mechanically inserted twist to increase yarn density, and thereby decrease yarn capacitance.

We have shown for our carbon nanotube hybrid muscles (*5*), which contain infiltrated volume-changing guest, and our polymer artificial muscles (*6*), that torsional actuation of the twisted fiber produces giant stroke tensile actuation for coiled muscles made from these fibers. The situation is like that for a coiled metal spring – a stretched coiled metal spring elongates because of torsional rotation of the wire within the spring. Like for these artificial muscles, we can use mandrel coiling to make coiled twistron harvesters that are named homochiral or heterochiral, depending upon whether the handedness of twist insertion and coil insertion are identical (as when increased twist insertion leads to yarn coiling) or different, respectively. Heating a two-end-tethered homochiral or heterochiral muscle causes yarn untwist, which increases yarn coiling (producing muscle contraction) or decreases yarn coiling (producing muscle expansion), respectively. Similarly, our coiled twistron energy harvesters produce a voltage when stretched, owing to the change in fiber twist and density generated by this tensile mechanical deformation.

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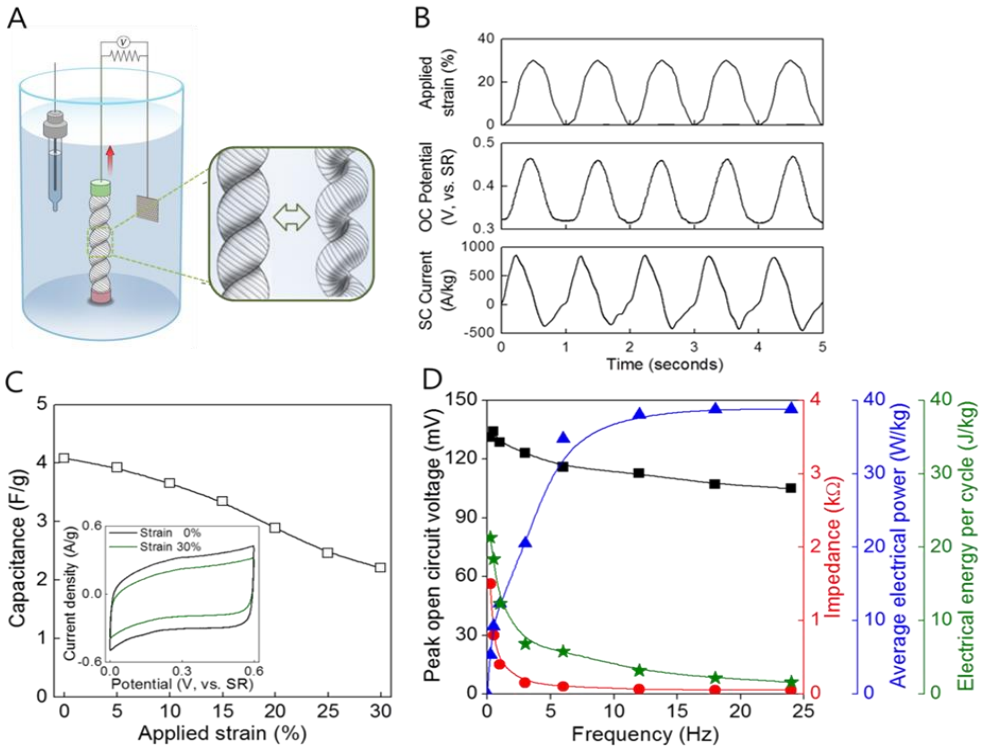

Figure 1. Stretch-driven energy harvesting from coiled twistron carbon nanotube yarns in aqueous electrolyte. (**A**) Schematic of stretching a coiled yarn inside a three electrode electrochemical system. (**B**) Typical open circuit voltage and short circuit current generated by mechanical strain. (**C**) Capacitance change induced by stretching. (**D**) Frequency dependence of the generated voltage, harvester impedance, average power and energy per cycle.

Consistent with our interpretation of a change in yarn twist as being the mechanistic process behind our successful use of coiled twistron yarns for energy harvesting, we have found that the application of a tensile stress to a homochiral yarn produces an opposite change in potential (versus a reference electrode) than does the application the same tensile stress to a heterochiral yarn. This result is extremely important, since it means that there is no need for a mechanical jig to convert an applied tensile stress to an elongation of one electrode and shortening of the other electrode, which would be the case if both electrochemical electrodes were either homochiral or heterochiral. We have found experimentally that this use of a mechanical harvesting cell comprising homochiral and heterochiral electrodes works, as predicted, to increase the power output from a coiled yarn twistron energy harvester when the applied stretch is in-phase for both electrodes. Importantly for some categories of applications, we have found that an elastomerically deformable solid-state electrolyte can replace the liquid electrolyte that we initially used for our twistron harvesters, so that a coiled yarn twistron tensile energy harvester can simply comprise electrolyte-coated homochiral and heterochiral yarn electrodes that are interconnected with an elastomeric solid-state gel electrolyte.

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The use of stress-induced capacitance changes provides one of the most attractive ways to convert mechanical energy into electrical energy by means of a compact harvester. In commercially utilized devices, which were developed at the Stanford Research Institute, a thin film of a rubber dielectric is sandwiched between two elastomeric electrodes. An applied voltage, typically several thousand volts, is used to inject a charge *Q* into this capacitor. Subsequent stretch of the highly elastomeric capacitor decreases the thickness of the rubber dielectric, via the Poisson ratio effect, thereby increasing capacitance. This stress-induced capacitance change produces a voltage change, which enables the harvesting of electrical energy.

This need for high applied voltages for mechanical energy harvesting using a dielectric capacitor poses practical problems. By stretching a twistron carbon nanotube supercapacitor electrode in salt water or other electrolytes, we surprisingly discovered that we can generate high electrical power output and high electrical energy per mechanical cycle without the need to externally apply a bias voltage. Our explanation is that the chemical potential difference between the electrode surface and the surrounding electrolyte results in either electron or hole injection into the electrode. As a result, simply immersing an electrode into an electrolyte generates an equilibrium charge state on the electrodes, which can be used for harvesting mechanical energy. We have shown that these charges are holes for low pH aqueous electrolytes (like 0.1 M HCl) and electrons for high pH electrolytes (like 0.1 M KOH).

In order to measure the equilibrium charge state of a CNT yarn harvester, it is necessary to know its potential of zero charge (pzc). Traditionally, direct measurement of the pzc has been difficult, and the results are often inaccurate. For our recent publication in *Science* (*7*), we developed a method to determine the electrochemical pzc, which utilizes the charge-state-dependent response of a CNT electrode to mechanical deformation. This method, hereafter referred to as piezoelectrochemical spectroscopy (PECS), is performed by characterizing an electrode by cyclic voltammetry (CV) while simultaneously applying a sinusoidal mechanical deformation to the electrode. By comparing this CV to a baseline scan without deformation, the alternating current (ac current) generated by the electrode was determined as a function of applied voltage. This is shown in Fig. 2, which overlays a CV scan taken at 0% strain with a CV taken during 5 Hz sinusoidal stretching between 0 and 10% strain. Using a lock-in technique, the magnitude and phase of the ac current with respect to the sinusoidal mechanical excitation are obtained as a function of voltage. From this relationship, the pzc is found at the potential of minimum ac current. This is further supported by the phase of the ac current with respect to the sinusoidal mechanical excitation. This phase inverts by 180^{o} at the pzc, which is consistent with the yarn having positive net charge at potentials above the pzc and negative charge below the pzc.

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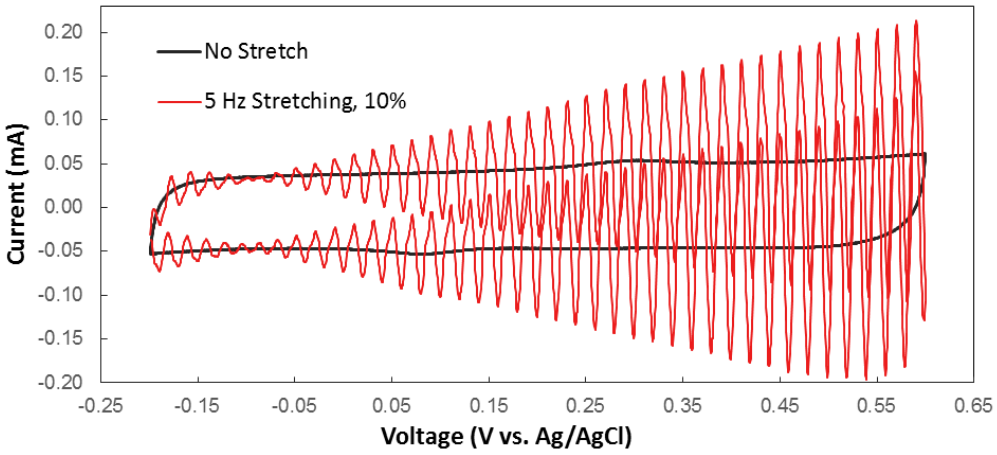

Figure 2. Measuring the potential of zero charge (pzc) by piezoelectrochemical spectroscopy (PECS). Cyclic voltammograms (taken at 100 mV/s in 0.1 M HCl) for a coiled twistron harvester are overlaid for the non-stretched state and during 5 Hz sinusoidal stretching by 10%. The pzc occurs when the stretch-induced oscillations in current are at a minimum (around -0.1 V)

Using 0.1 M HCl as the electrolyte and a sinusoidal mechanical stretch of 50%, the realized peak gravimetric power output per harvester weight reached a remarkable 250 W/kg, and the realized mechanically-induced changes in capacitance and open circuit voltage exceeded 30% and 240 mV, respectively. This peak power is over a hundred times larger than for any previously reported mechanical-energy-harvesting yarn or fiber. Figure 3 compares the gravimetric peak power and frequency normalized peak power (which is related to the electrical energy per cycle) for our twistron yarns with that for alternative technologies. Most of these generic types of devices are centuries or many decades old. Nevertheless, for the frequency range that is especially important for many applications (2 Hz to 30 Hz), no other energy harvesting technology provides as high a gravimetric output power as our twistron harvesters.

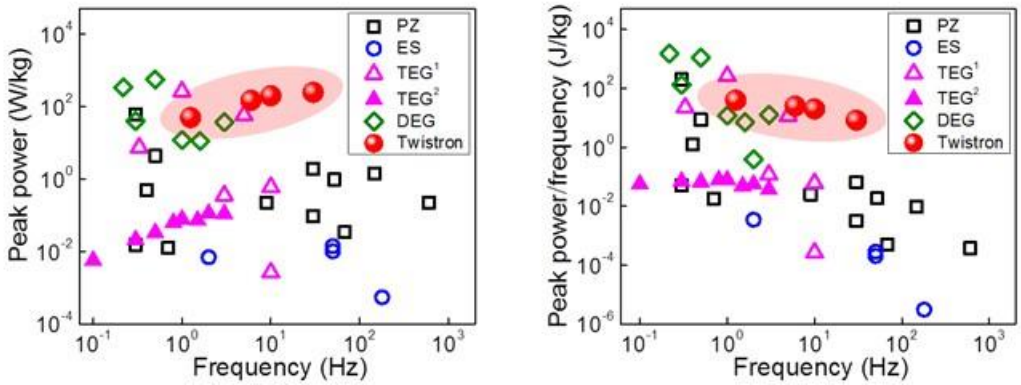

Figure 3. Peak power (left) and frequency-normalized peak power (right) versus the frequency at which this peak power was obtained for present and prior-art technologies for piezoelectric (PZ), electrostatic (ES), triboelectric (TEG), and dielectric elastomer (DEG) generators.

3. PROJECT SUPPORTED ARCHIVAL PUBLICATIONS

1. “Hierarchically buckled sheath-core fibers for superelastic electronics, sensors, and muscles”, Z. F. Liu, S. Fang, F. A. Moura, J. N. Ding, N. Jiang, J. Di, M. Zhang, X. Lepró, D. S. Galvão, C. S. Haines, N. Y. Yuan, S. G. Yin, D. W. Lee, R. Wang, H. Y. Wang, W. Lv, C. Dong, R. C. Zhang, M. J. Chen, Q. Yin, Y. T. Chong, R. Zhang, X. Wang, M. D. Lima, R. Ovalle-Robles, D. Qian, H. Lu, R. H. Baughman, *Science* **349**, 400-404 (2015).

2. “Harvesting temperature fluctuations as electrical energy using torsional and tensile polymer muscles”, S. H. Kim, M. D. Lima, M. E. Kozlov, C. S. Haines, G. M. Spinks, S. Aziz, C. Choi, H. J. Sim, X. Wang, H. Lu, D. Qian, J. D. W. Madden, R. H. Baughman and S. J. Kim, *Energy & Environmental Science* **8**, 3336-3344 (2015).

3. “High performance electrochemical and electrothermal artificial muscles from twist-spun carbon nanotube yarn”, J. A. Lee, R. H Baughman and S. J. Kim, *Nano Convergence* 2015, 2:8 doi:10.1186/s40580-014-0036-0.

4. “Stretchable, Weavable Coiled Carbon Nanotube/MnO_2/Polymer Fiber Solid-State Supercapacitors”, 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, *Scientific Reports* | 5 : 9387 | DOI: 10.1038/srep09387.

5. "Straining to expand entanglements”, R. H. Baughman and A. F. Fonseca, *Nature Materials* **15**, 7-8 (2016).

6. “Bio-Inspired Polymer Artificial Muscles”, S. Naficy, G. M Spinks, R. H. Baughman, Chapter 13, pp. 429-459, *Bioinspired Polymers*, Editors N. Bruns and A. F. M. Kilbinger, RSC Polymer Chemistry Series (2016).

7. “High-efficiency electrochemical thermal energy harvester using carbon nanotube aerogel sheet electrodes”, H. Im, T. Kim, H. Song, J. Choi, J. S. Park, R. Ovalle-Robles, H. D. Yang, K. D. Kihm, R. H. Baughman, H. H. Lee, T. J. Kang, and Y. H. Kim, *Nature Communications*, 7:10600 doi: 10.1038/ncomms10600 (2016).

8. "Elastomeric and Dynamic MnO2/CNT Core-Shell Structure Coiled Yarn Supercapacitor", C. Choi, H. J. Sim; G. M. Spinks, X. Lepró; R. H. Baughman, S. J. Kim, *Advanced Energy Materials* **6**, 1502119 (2016). Selected as a cover for the hard cover version.

9. “Biothermal sensing of a torsional artificial muscle”, S.-H. Lee, T. H. Kim, M. D. Lima, R. H. Baughman, and S. J. Kim, *Nanoscale* **8**, 3248-3253 (2016).

10. “Carbon Nanotube Yarn-Based Glucose Sensing Artificial Muscle”, J. Lee, S. Ko, C. H. Kwon, M. D. Lima, R. H. Baughman, S. J. Kim, *Small* **12**, 2085-2091 (2016), selected as one of the journals covers.

11. “Highly stretchable hybrid nanomembrane supercapacitor”, K. J. Kim, J. A. Lee, M. D. Lima, R. H. Baughman, S. J. Kim, *Royal Society of Chemistry Advances* **6**, 24756-24759 (2016).

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4. PATENT FILINGS ON PROJECT-SUPPORTED WORK

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