A Self-Charging Power Unit by Integration of a Textile Triboelectric Nanogenerator and a Flexible Lithium-Ion Battery for Wearable Electronics

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Wearable energy devices are receiving intensive research endeavor, aiming at powering a variety of flexible electronics such as wearable smart phones, healthcare sensors, and smart uniforms.[1] While the flexibility or bendability has been demonstrated in displays,[2] light-emitting diodes,[3] sensors,[4] and flexible circuits,[5] the use of traditional rigid battery packs as a power source remains a bottleneck hindering the progress of wearable electronics. Furthermore, the long-standing challenge in improving the energy density of the battery has not yet been well addressed.[6] The consequential heavy weight, bulky volume, and frequent charging of a battery make portable electronics uncomfortable or inconvenient to be worn on the curved human body. Therefore, in addition to improving the flexibility of battery, the solution also lies in the proper integration of wearable energy-harvesting and energy-storing devices into a self-sustainable or self-sufficient power system.

The triboelectric nanogenerator (TENG) is a newly developed energy-harvesting technology that converts mechanical energy into electric power with a coupled effect of contact-electrification and electrostatic induction.[7] It is promising for applications both in scavenging small mechanical energy and large-scale energy generation, because of its high efficiency, low-cost, environmental friendliness, and universal availability.[7b] Various structures have been designed to harvest different types of energies such as the wind,[8] water-waves,[9] raindrops,[10] and human motion.[11] Due to the universal existence of the triboelectricity, the materials choice of the TENG is enormous, as long as the triboelectric negativity is appropriately considered,[7b] ensuring the feasibility in designing a highly flexible or wearable TENG to harvest the energy of daily human motions and to power wearable electronics. Though several recent studies have reported flexible and wearable TENGs based on thin polymer and metal films,[11c,12] further research is still urgently required to design textile-based TENGs that are light, soft, washable, breathable, stretchable, and thus directly wearable as a cloth.

On the contrary, rechargeable batteries are still indispensable in portable electronics, considering the discontinuity of the energy source (i.e., solar, thermal, wind, and mechanical energy) of most energy harvesters. In order to improve the flexibility of batteries, it is essential to substitute the rigid package and current collector of commercial batteries with bendable or stretchable counterparts.[1,13] Recent research has reported paper or textile batteries with the utilization of graphene,[14] carbon nanotubes (CNT),[15] or carbon nanofiber cloth[16] as the flexible substrate, whereas the scale-up difficulty and high cost of these materials impede their practical commercialization.

Herein, we designed a wearable power unit by integrating a whole-textile TENG-cloth and a flexible lithium-ion battery (LIB) belt. Common flexible but insulating polyester fabrics were transformed into conductive with an electroless plating of a conformal Ni film, which were then utilized both as electrodes in the TENG-cloth and as current collectors in the LIB belt. The TENG-cloth demonstrated the capability of converting the mechanical energy of various human motions into electricity when being worn at different positions on the human body; the LIB belt showed decent electrochemical performances even being severely folded at 180° for 30 times. Furthermore, the LIB belt was charged by the TENG-cloth for 3 cycles, and powered a heartbeat meter strap capable of remote communication with a smart phone, verifying the viability of the whole-wearable and self-charging power unit for future wearable smart electronics.

As the conductive electrode is one of the key components in a TENG, it is crucial to develop a soft and wearable conductor for wearable TENG. Common soft polyester fabric was selected as the starting substrate, and was consecutively coated with conductive Ni film (Ni-cloth) and insulating parylene film (parylene-cloth), as schematically illustrated in **Figure 1**a. Due to the difficulty in handling individual polyester microwire, belt-type Ni-cloth, and parylene-cloth (5-mm wide) were used as the building block (see Figure 1a,b), and finally woven into a 5 cm × 5 cm TENG-cloth (see Figure 1a,c). All the Ni-cloth belts were connected together as one electrode of the TENG, while all the parylene-cloth belts were connected as the other. After the Ni-coating, white polyester cloth changes into silver; while parylene layer is relatively transparent (see Figure 1b). The woven

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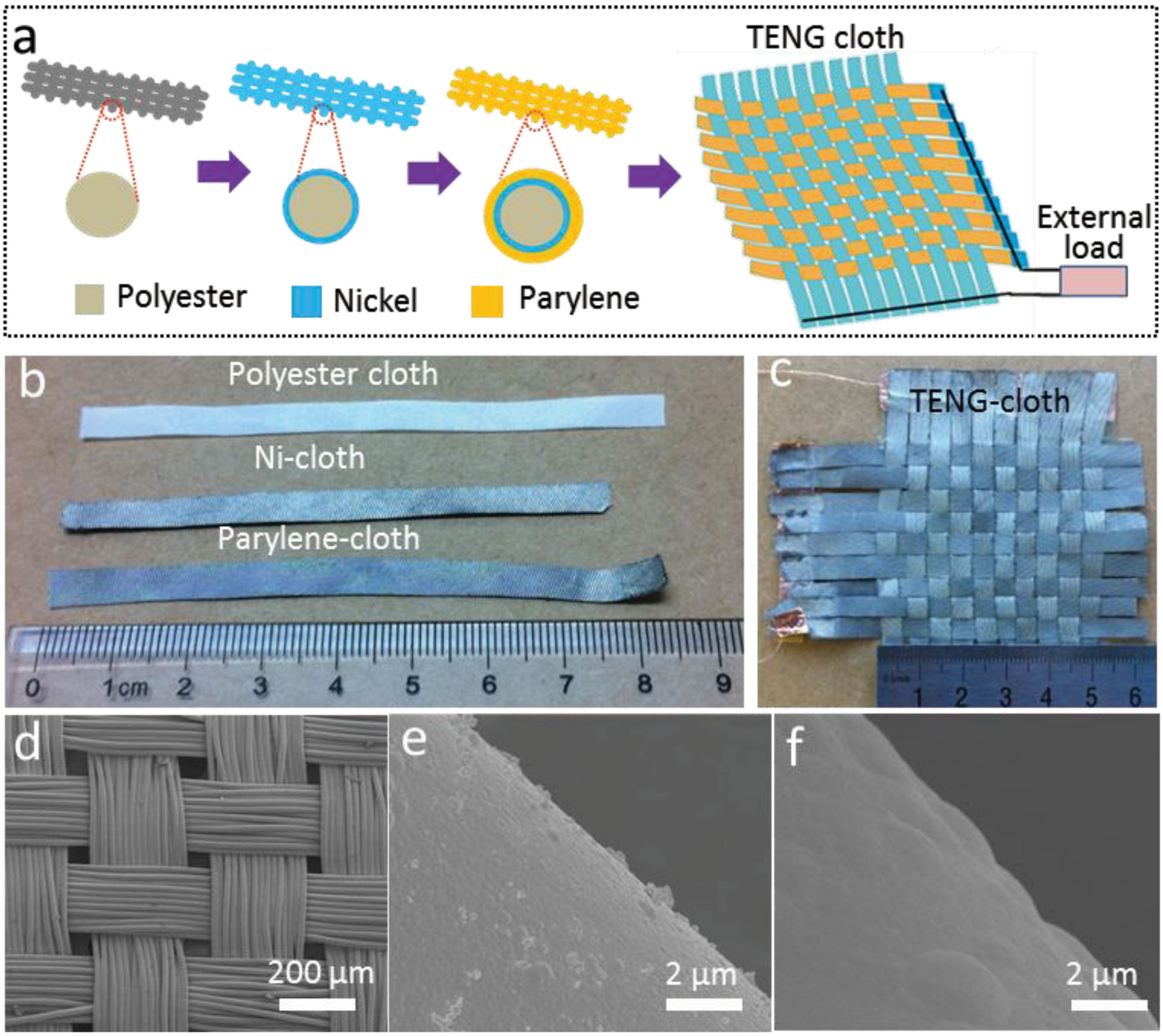

Figure 1. The fabrication of triboelectric nanogenerator cloth (TENG-cloth). a) Schematic illustration of the fabrication of TENG-cloth. b) An optical image of pristine polyester cloth, Ni-cloth and parylene-cloth. The Ni-cloth is coated with conductive Ni coating by an electroless deposition; the parylene-cloth has an insulating parylene film on top of the Ni coating. c) An optical image of the TENG-cloth fabricated by weaving Ni-cloth and parylene-cloth. SEM images of d) pristine polyester cloth, e) Ni-cloth, and f) parylene-cloth.

TENG-cloth textile retains the mechanical flexibility, air-breathability, water-washability, and thus comfortability of the original polyester cloth. Figure 1d shows the SEM image of the pristine polyester cloth with a woven structure of polyester microwires. After the electroless coating of Ni, the surface of the polyester cloth was coated with a conformal Ni layer with nanoscale roughness (see Figure 1e). The resistance of a 0.5 cm × 10 cm Ni-cloth is measured to be several ohms, comparable with typical metal foils and more conductive than reported CNT or graphene papers.[17] Meanwhile, this coating method is low-cost and suitable for scale-up, and we can easily coat the polyester cloth with arbitrary size and shape in a short time and at low temperature. In contrast, the expensive synthesis of CNT or graphene by chemical vapor deposition at very high temperature and extra efforts in dispersing them in solvents make them difficult for large-scale application. Figure 1f shows a relatively smooth layer of parylene film covering the underneath Ni film after the chemical vapor deposition of parylene. It should be noted that coating methods used for Ni and parylene both produced conformal layers that cover the wavy surface of the textile substrate.

In order to elucidate the working principle, the output characteristics of the fabricated TENG-cloth at a TENG-cloth–TENG-cloth contact–separation (C–S) mode were characterized, as shown in **Figure 2**. The releasing and pressing of two pieces of TENG-cloths can be simplified into the contact–separation between a parylene-cloth wire and a Ni-cloth wire, since all the parylene-cloth wires and Ni-cloth wires are respectively connected together as two electrodes, as schematically illustrated in Figure 2a. Contact electrification, i.e., electron transfer from tribopositive Ni film to trobonegative parylene film, occurs once

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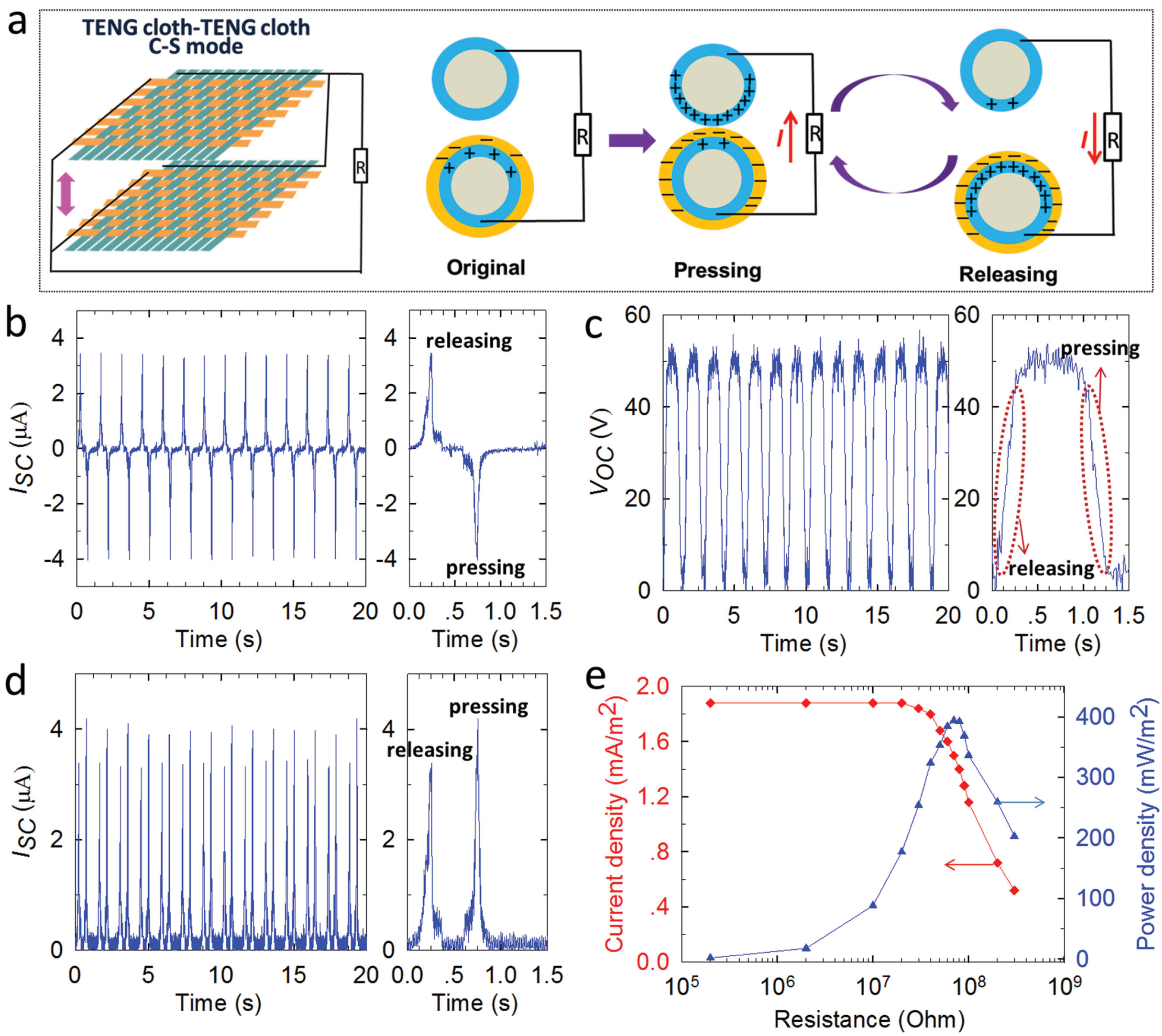

Figure 2. The output of the wearable TENG-cloth. a) Schematic illustration of the working mechanism of the wearable TENG in TENG-cloth–TENG-cloth contact–separation mode. b–d) The output short-circuit current (b); open-circuit voltage (c); and rectified short-circuit current (d) of the TENG. e) The variation of current density and power density of the TENG with the external load resistance.

two TENG-cloths are brought into close contact. This charge separation will create an electric potential difference (EPD) between the two electrodes: $U_{EPD} = -\sigma d/\varepsilon_o$, where σ is the triboelectric charge density, ε_o is the vacuum permittivity, and d is the distance between two electrodes.[7b] When the TENG is being released, the open-circuit voltage (V_{oc}) increases as the EPD is increased, while V_{oc} decreases when the TENG is pressed (see Figure 2c). When the TENG is shortened, the EPD will drive the flow of electrons between two electrodes through the external circuit, creating two current pulses (I_{sc}) with opposite directions when being released and pressed (see Figure 2b). The maximum V_{oc} and I_{sc} is 50 V and 4 μA, respectively, which is dramatically improved comparing with previously reported textile nanogenerators made of CNT and Ag wires.[18] With a rectifier, the negative current can be reversed into positive, as shown in Figure 2d.

Figure 2e shows the variation of areal peak current density and power density versus the external loading resistance. The power density is calculated by $W = (I_{peak}^2 R)/A$, where A is the area of the TENG-cloth and R is the external load resistance. The current density shows no obvious decrease until the external resistance is increased to about 60 MΩ, indicating that the TENG-cloth is suitable for a constant current source.[19] The peak power density reaches the maximum of 393.7 mW m^{-2} when the external resistance is about 70 MΩ. Given a human body of surface area of roughly 1.44 m^2 (0.9 m chest perimeter, 0.7 m upper body height, 0.45 m leg perimeter, and 0.9 m leg length), the ideal peak power generation can be 566.9 mW. If the motion or working time of a human body is 6 h per day, the peak energy generated by human motion can be 3.4 W h, which is able to fully charge a battery with 3.4 V operation voltage and 1000 mA h capacity, close to that of a battery of a smart phone.

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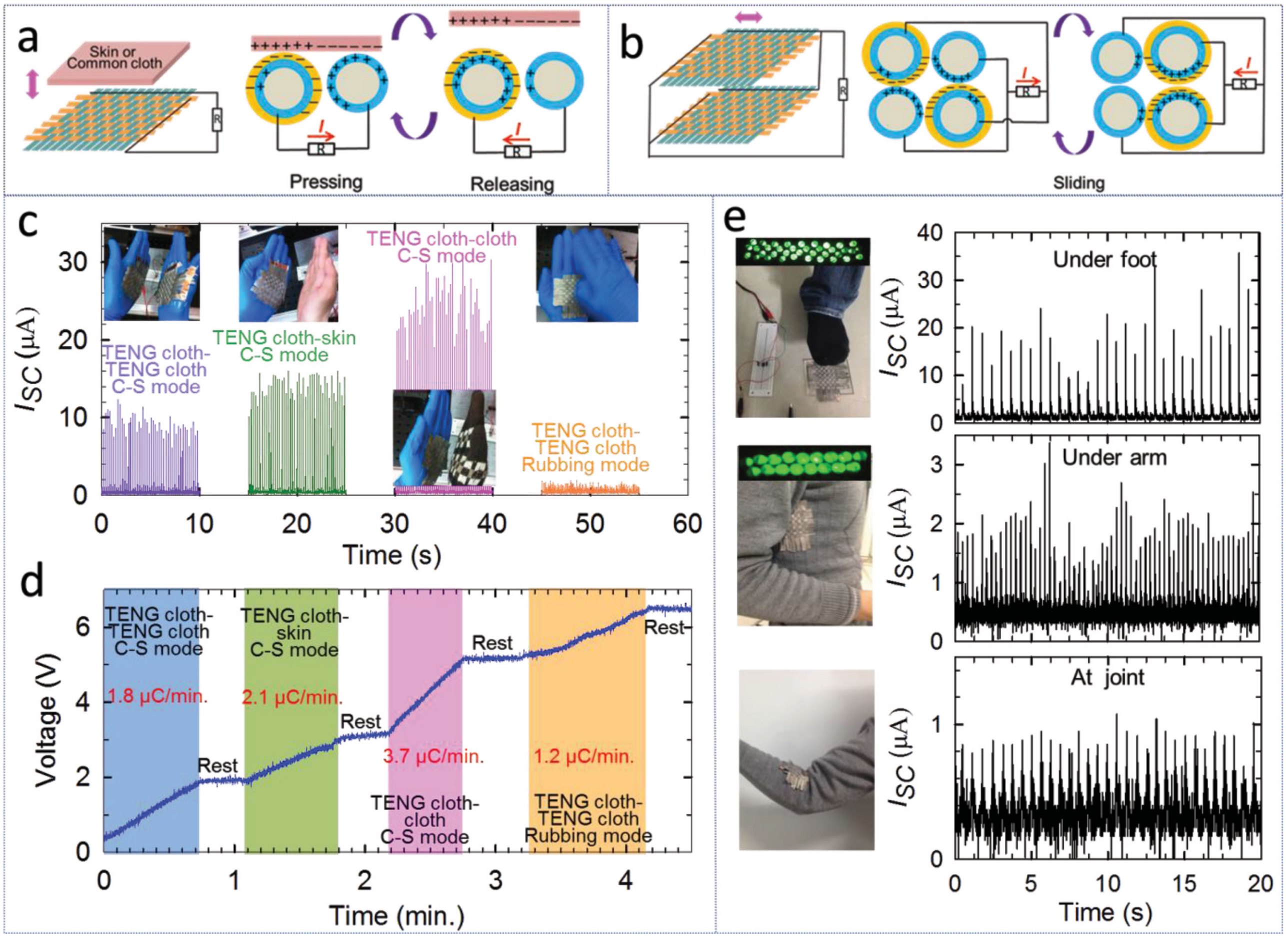

Figure 3. Harvesting mechanical energy of different human motions by the TENG-cloth. a,b) Scheme of mechanisms of the TENG-cloth working at different modes. c) The rectified short-circuit current and corresponding optical images (insets of c) of TENG-cloth at different modes. d) The voltage profile of a capacitor (100 V and 1 μF) charged by the TENG-cloth at different modes. e) The optical images and corresponding short currents when the TENG-cloth was worn at different positions of human body, from top to bottom: under foot, under arm, and at elbow joint. The inset also shows 37 and 17 LEDs lit by the TENG-cloth when being worn under the foot and arm, respectively.

Though not all parts of human body are in motion, the TENG-cloth is still promising to compensate the energy consumption of smart electronics so as to elongate their standby time.

The versatility of the TENG-cloth in scavenging energy of various types of human motions was also demonstrated, as shown in **Figure 3**. Figure 3a,b elucidate the operation mechanisms of TENG-cloth in vertical C–S motion with the human skin or other common cloths, and two TENG-cloths in horizontal sliding motion, respectively. As shown by the inset optical photos in Figure 3c, the TENG-cloth was attached to the hand to mimic four modes of relative motions of human body: TENG-cloth–TENG-cloth C–S mode, TENG-cloth–skin C–S mode, TENG-cloth–cloth C–S mode, and TENG-cloth–TENG-cloth rubbing mode. The corresponding rectified peak short currents I_{sc} were measured to be around ≈10, 15, 20, 1.5 μA, respectively (see Figure 3c). Figure 3d shows the voltage profile of a capacitor (1 μF and 100 V) charged by the TENG under these four modes of energy generation. The slope of the charge accumulation was measured to be 1.8, 2.1, 3.7, and 1.2 μC min^{-1}, respectively (calculated by $\Delta Q = C\Delta V$). It should be noted that the charge accumulation rate of rubbing mode is comparable with three C–S modes though its peak current is an order smaller, due to the increased frequency by introducing each building block (parylene-cloth wire and Ni-cloth wire) as a segment. Similar improvements have been reported in our previous publications that segmentation design can increase the frequency and output power.[20] By narrowing the width or diameter of the woven belts or wires into the microscale, it is promising to further improve the output of the TENG-cloth under rubbing mode.

Thanks to the above-demonstrated versatility, the TENG-cloth can be worn at nearly every position of human body as long as there is relative motion (either C–S or rubbing) of TENG-cloth with TENG-cloth, common cloth, or human skin. As shown in Figure 3e, the TENG-cloth was worn under foot, under arm, and at the elbow joint (see photos in Figure 3e). The peak rectified short currents (see plots in Figure 3e) generated by foot pressing, arm swinging, and elbow bending are ≈20, 2, and 0.8 μA, respectively. The TENG-cloth worn under foot and arm can also light 37 and 17 green light-emitting diodes (LEDs), respectively (see insets in photos in Figure 3e). Video S1 (Supporting Information) records that 37 LEDs were lit by the TENG-cloth worn

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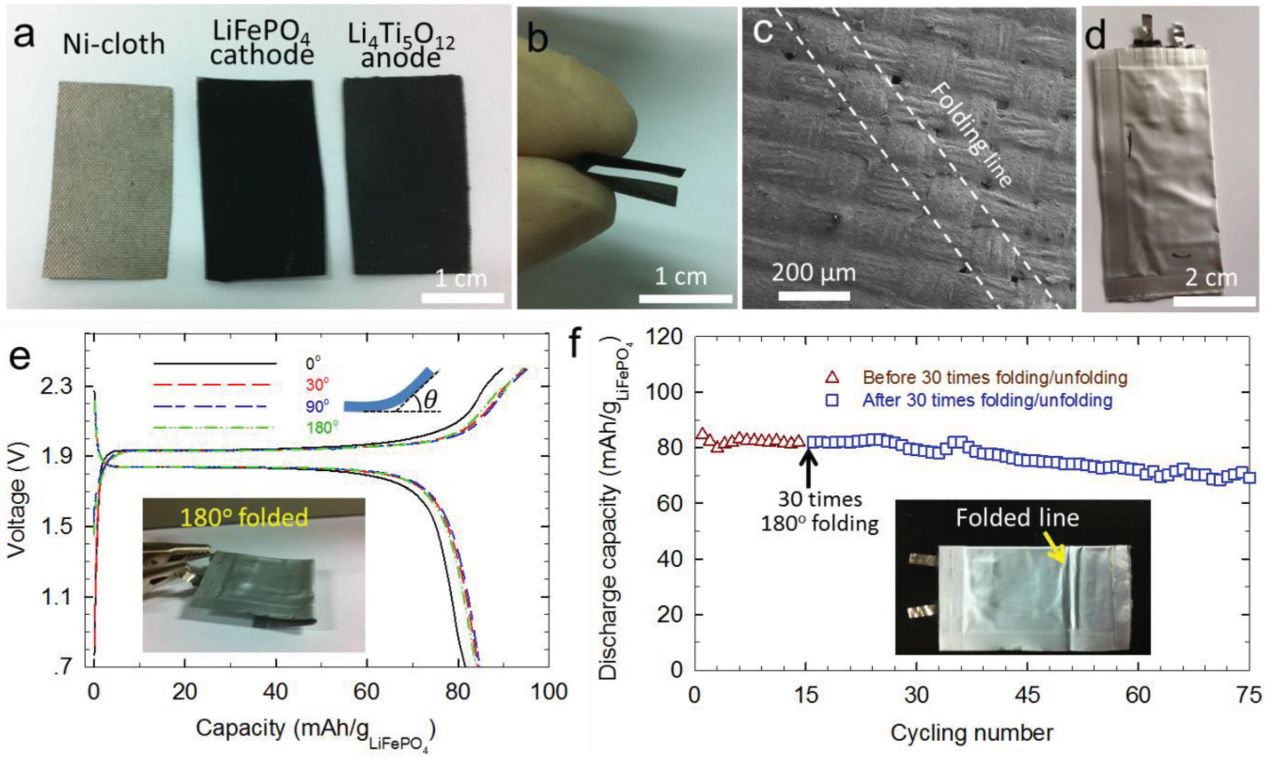

Figure 4. The fabrication and performances of flexible LIB belt. a) An optical photo of pristine Ni-cloth substrate, $LiFePO_4$-coated cathode, and $Li_4Ti_5O_{12}$-coated anode. b) A photo of a bended anode. c) SEM image of an anode film after a complete folding. d) A photo of a fabricated LIB belt. e) Voltage profiles of LIB belt bended at different angles. The inset of (e) shows the 180°-folded LIB belt during test. f) The cycling performances of the LIB belt before and after 30 times of 180° folding/unfolding. The inset in (f) indicates the folded line after the folding/unfolding cycles.

under arm, further confirming the viability of energy generation by the TENG-cloth.

Considering the discontinuity of human motion and the pulse output of TENG-cloth, wearable energy-storage devices are still necessary so that the energy generation and storage can be integrated to achieve our goal of self-charging power unit for wearable electronics. As discussed above, the key to fabricating a highly flexible LIB is to utilize soft or flexible current collectors and battery packages. In our design, the conductive Ni-coated polyester textile (i.e., Ni-cloth) was utilized as current collectors in both the cathode and the anode, and a flexible pouch cell was assembled, as shown in **Figure 4**. Active slurries of $LiFePO_4$ and $Li_4Ti_5O_{12}$ were coated on the Ni-cloth as the cathode and the anode, respectively (see Figure 4a). The microscale woven feature of the textile (see Figure 1d) and the nanoscale roughness of the Ni coating (see Figure 1e) promote the intimate contact and adhesion of active layers with the conductive Ni film. Meanwhile, the excellent flexibility of the textile electrode is retained, as demonstrated by facile 180° bending of one electrode in Figure 4b. Even after a complete folding of the textile electrode, no peel-off of the active materials can be observed, as indicated by the white strap in Figure 4c, confirming the intimate adhesion between the active materials and the textile current collectors. Figure 4d shows a finally assembled belt-type pouch cell with textile $LiFePO_4$ cathode, textile $Li_4Ti_5O_{12}$ anode, and a soft Celgard separator.

Figure 4e shows the charge/discharge profiles at 0.5 C rate (1 C = 170 mA g^{-1} of $LiFePO_4$) of the LIB belt folded at different angles ranging from 0° to 180°. At the original state (i.e., 0° bending), the LIB shows a discharge voltage plateau of ≈1.8 V, a charge voltage plateau of ≈1.9 V, and a discharge capacity of 81 mA h g^{-1} normalized by the weight of cathode $LiFePO_4$. Upon bending at 30°, 90°, and 180°, no degradation of battery performances can be observed. In contrast, the capacity is slightly increased comparing with that at original state, presumably because that the anode and cathode are pressed closer during bending. At 180° bending, the LIB belt is actually folded completely (see the inset in Figure 4e). After 30 times of 180° complete folding, the LIB belt still exhibits highly stable cycling performances, achieving 85.4% capacity retention in the subsequent 60 cycles of charge/discharge at 0.5 C rate (see Figure 4f). A residual line can be clearly observed in the LIB belt after the severe deformation for 30 cycles, as indicated in the inset in Figure 4f. The excellent flexibility and stable electrochemical performances of the LIB belt is because that all components in the pouch cell are flexible, which ensures the feasibility of wearing this LIB pouch belt as wrist straps, a waist belt, etc.

Figure 5 demonstrates the self-charging power unit by integrating the TENG-cloth as energy generation device and the LIB belt as energy storage device. A prototype of the power system is shown in Figure 5a, where a heartbeat meter strap worn at the chest is powered by a LIB belt, which can be further charged or compensated by a TENG-cloth worn under the arm. The heartbeat meter has Bluetooth function, so that a remote smart phone can record and analyze the physiological information of human during sports or daily life. Figure 5b shows

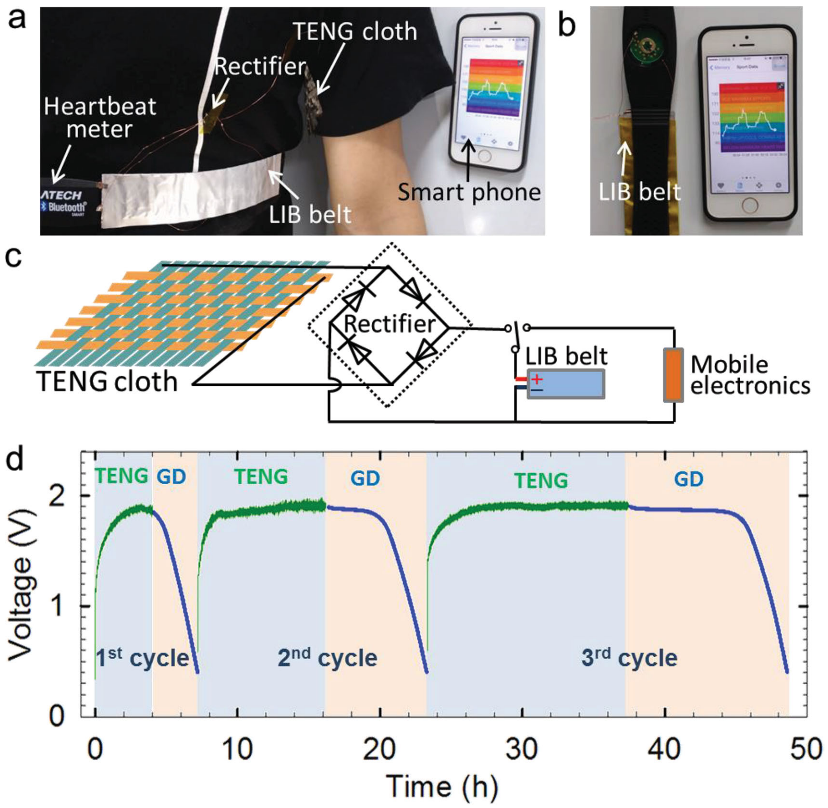

Figure 5. Self-charging power unit. a) An optical image of the integrated self-charging power system that harvests mechanical energy of human motion with TENG-cloth, stores the energy with LIB belt, and then powers heartbeat meter strap, which has remote communication with a smart phone. b) The rear side of heartbeat meter, indicating that its original coin cell was replaced by the LIB belt. c) The equivalent electrical circuit of the self-charging power system. d) The voltage profiles of the LIB belt charged by the TENG-cloth and galvanostatically discharged (GD) at 1 μA for 3 cycles.

the rear side of the heartbeat strap, confirming that its original rigid coin cell is replaced by our wearable LIB belt. The equivalent electric circuit of the whole system is shown in Figure 5c. Video S2 (Supporting Information) records the remote communication of a smart phone with a heartbeat meter strap, which is powered by our self-charging and wearable power unit. This power unit can be easily modified for many other wearable smart electronics, such as smart watches and smart glasses.

To further verify the capability and stability of the wearable TENG-cloth in charging LIB belt, a LIB belt was charged by the TENG-cloth and subsequently discharged galvanostatically (GD) at 1 μA constant current for 3 cycles, as shown in Figure 5d. A linear motor was utilized to mimic the TENG-cloth–TENG-cloth C–S mode motion of human at 0.7 Hz low frequency during the charge process. The voltage of the LIB belt increases rapidly to the operational voltage (≈1.9 V) upon the charging by the TENG-cloth. The charging time for the first, second, and third cycle is 4, 9, and 14 h, respectively. The corresponding discharge capacities are 1.3, 2.8, and 4.4 mA h m^{-2}, respectively, when being normalized by the area of the TENG-cloth. During sports, the motion frequency of human body is actually much larger than 1 Hz, and thus higher energy generation can be expected. This energy is enough to power many small healthcare electronics (e.g. heartbeat meter, pedometer, pulse meter, body temperature meter), making the self-charging and wearable power unit possible to diminish or even eliminate the battery charge by a bulky household battery charger.

In conclusion, we have developed a self-charging power unit for smart electronics by integrating a textile TENG-cloth as an energy harvester and a flexible LIB belt as energy storage. The whole-textile TENG-cloth can be worn at many different positions of the human body (e.g., under the foot, under the arm, and at a joint), due to its versatility in scavenging energies of various modes of human motions. Excellent flexibility and stable electrochemical performances of the LIB belt was achieved even when the LIB belt was completely folded at 180° for 30 times, owing to the utilization of conductive Ni-cloth textile as current collector in both cathode and anode, and the use of Al pouch as package. The electric energy converted from the daily human motion by the TENG-cloth was demonstrated to be able to charge the LIB belt, which then was able to power a heartbeat meter with remote communication with a smart phone. The stability of the power unit was further confirmed by charging the LIB with TENG-cloth and subsequently galvanostatic discharging for 3 cycles. The viability of our wearable and self-charging power unit provides potential solution to pave the way for the progress of wearable/flexible electronics in the near future.

Experimental Section

Preparation of TENG-Cloth: Conductive Ni-cloth textile was prepared by an electroless plating of Ni on common polyester cloth. Polyester cloth was first cleaned with abundant acetone and deionized (DI) water by a bath sonicator. Subsequently, it was sensitized by aqueous solution with 10 g L^{-1} $SnCl_2$ and 40 mL L^{-1} 38% HCl, and then activated with an aqueous solution with for 0.5 g L^{-1} $PdCl_2$ and 20 mL L^{-1} 38% HCl at room temperature for 10 min, respectively. After rinsing in DI water, the seeded polyester cloth was immersed in a 0.1 M $NiSO_4$ aqueous solution for electroless plating at 80° for 10 min. The PH was adjusted to 10 by 10% NaOH solution. After the coating, the Ni-cloth was washed with DI water and then dried in vacuum oven.

Parylene-cloth was prepared by chemical vapor deposition of parylene on the conductive Ni-cloth with Dichloro-[2,2]-paracyclophane as the source. TENG-cloth was woven with ten Ni-cloth belts as longitude lines and ten parylene-cloth belts as latitude lines. All the TENG-cloth belts were connected together by copper wire as one electrode, and all the Ni-cloth belts connected as another electrode.

Preparation of Flexible LIB Belt: Ni-cloth was used as current collectors in both cathode and anode. $LiFePO_4$ (MTI, Inc.) and $Li_4Ti_5O_{12}$ (MTI, Inc.) were used as active materials for cathode and anode, respectively. Active materials, carbon black, and PVDF with the weight ratio of 7:2:1 were thoroughly mixed in NMP to prepare slurries, which were subsequently pasted onto the Ni-cloth by a doctor blade. Then, electrodes were annealed at 120° for 12 h in a vacuum oven. The areal weight of active

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materials is about 4 mg cm^{-2} in the final electrodes. The flexible LIB belt was assembled using an Al pouch as package, Celgard 2325 as separator, and 1 M $LiPF_6$ in EC:DMC (1:1 by vol.) as electrolyte. The weight ratio of $LiFePO_4$ to $Li_4Ti_5O_{12}$ in a LIB cell is about 1.2.

Characterizations and Measurements: The output short current and open-circuit voltage of the TENG-cloth were measured by a Stanford low-noise current preamplifier (Model SR570) and a Keithley electrometer (Keithley 6514), respectively. The TENG-cloth was attached onto a linear motor to mimic human motions for the measurement. The LIB belt was cycled at 0.5 C rate (1 C = 170 mA h g^{-1} of $LiFePO_4$) by a galvanostat (LAND CT2001A). For the demonstration of self-charging power unit, the charge and discharge profile of LIB belt was recorded by Keithley 6514 and LAND CT2001A, respectively. Scanning electron microscopy (SEM) was taken with a Hitachi SU8200.

Supporting Information

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

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[1] X. Wang, X. Lu, B. Liu, D. Chen, Y. Tong, G. Shen, *Adv. Mater.* **2014**, *26*, 4763.
[2] J. A. Rogers, Z. Bao, K. Baldwin, A. Dodabalapur, B. Crone, V. R. Raju, V. Kuck, H. Katz, K. Amundson, J. Ewing, P. Drzaic, *Proc. Natl. Acad. Sci. USA* **2001**, *98*, 4835.
[3] M. S. White, M. Kaltenbrunner, E. D. Glowacki, K. Gutnichenko, G. Kettlgruber, I. Graz, S. Aazou, C. Ulbricht, D. A. M. Egbe, M. C. Miron, Z. Major, M. C. Scharber, T. Sekitani, T. Someya, S. Bauer, N. S. Sariciftci, *Nat. Photonics* **2013**, *7*, 811.
[4] a) D.-H. Kim, N. Lu, R. Ghaffari, Y.-S. Kim, S. P. Lee, L. Xu, J. Wu, R.-H. Kim, J. Song, Z. Liu, J. Viventi, B. de Graff, B. Elolampi, M. Mansour, M. J. Slepian, S. Hwang, J. D. Moss, S.-M. Won, Y. Huang, B. Litt, J. A. Rogers, *Nat. Mater.* **2011**, *10*, 316; b) D.-H. Kim, N. Lu, R. Ma, Y.-S. Kim, R.-H. Kim, S. Wang, J. Wu, S. M. Won, H. Tao, A. Islam, K. J. Yu, T.-i. Kim, R. Chowdhury, M. Ying, L. Xu, M. Li, H.-J. Chung, H. Keum, M. McCormick, P. Liu, Y.-W. Zhang, F. G. Omenetto, Y. Huang, T. Coleman, J. A. Rogers, *Science* **2011**, *333*, 838.
[5] K. Takei, T. Takahashi, J. C. Ho, H. Ko, A. G. Gillies, P. W. Leu, R. S. Fearing, A. Javey, *Nat. Mater.* **2010**, *9*, 821.
[6] a) X. Pu, G. Yang, C. Yu, *Adv. Mater.* **2014**, *26*, 7456; b) X. Pu, G. Yang, C. Yu, *Nano Energy* **2014**, *9*, 318.
[7] a) F. R. Fan, Z. Q. Tian, Z. Lin Wang, *Nano Energy* **2012**, *1*, 328; b) Z. L. Wang, *ACS Nano* **2013**, *7*, 9533.
[8] a) Y. Xie, S. Wang, L. Lin, Q. Jing, Z.-H. Lin, S. Niu, Z. Wu, Z. L. Wang, *ACS Nano* **2013**, *7*, 7119; b) Y. Yang, G. Zhu, H. Zhang, J. Chen, X. Zhong, Z.-H. Lin, Y. Su, P. Bai, X. Wen, Z. L. Wang, *ACS Nano* **2013**, *7*, 9461.
[9] a) G. Zhu, Y. Su, P. Bai, J. Chen, Q. Jing, W. Yang, Z. L. Wang, *ACS Nano* **2014**, *8*, 6031; b) Z.-H. Lin, G. Cheng, L. Lin, S. Lee, Z. L. Wang, *Angew. Chem. Int. Ed.* **2013**, *52*, 12545.
[10] Z.-H. Lin, G. Cheng, S. Lee, K. C. Pradel, Z. L. Wang, *Adv. Mater.* **2014**, *26*, 4690.
[11] a) Y. Xie, S. Wang, S. Niu, L. Lin, Q. Jing, J. Yang, Z. Wu, Z. L. Wang, *Adv. Mater.* **2014**, *26*, 6599; b) T.-C. Hou, Y. Yang, H. Zhang, J. Chen, L.-J. Chen, Z. Lin Wang, *Nano Energy* **2013**, *2*, 856; c) G. Zhu, P. Bai, J. Chen, Z. Lin Wang, *Nano Energy* **2013**, *2*, 688.
[12] a) H. Zhang, Y. Yang, T.-C. Hou, Y. Su, C. Hu, Z. L. Wang, *Nano Energy* **2013**, *2*, 1019; b) S. Jung, J. Lee, T. Hyeon, M. Lee, D.-H. Kim, *Adv. Mater.* **2014**, *26*, 6329.
[13] a) A. M. Gaikwad, B. V. Khau, G. Davies, B. Hertzberg, D. A. Steingart, A. C. Arias, *Adv. Energy Mater.* **2015**, *5*, DOI: 10.1002/aenm.201401389; b) Q. Cheng, Z. Song, T. Ma, B. B. Smith, R. Tang, H. Yu, H. Jiang, C. K. Chan, *Nano Lett.* **2013**, *13*, 4969; c) S. Xu, Y. Zhang, J. Cho, J. Lee, X. Huang, L. Jia, J. A. Fan, Y. Su, J. Su, H. Zhang, H. Cheng, B. Lu, C. Yu, C. Chuang, T.-i. Kim, T. Song, K. Shigeta, S. Kang, C. Dagdeviren, I. Petrov, P. V. Braun, Y. Huang, U. Paik, J. A. Rogers, *Nat. Commun.* **2013**, *4*, 1543.
[14] N. Li, Z. P. Chen, W. C. Ren, F. Li, H. M. Cheng, *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 17360.
[15] L. Hu, H. Wu, F. La Mantia, Y. Yang, Y. Cui, *ACS Nano* **2010**, *4*, 5843.
[16] B. Liu, J. Zhang, X. Wang, G. Chen, D. Chen, C. Zhou, G. Shen, *Nano Lett.* **2012**, *12*, 3005.
[17] a) L. Hu, M. Pasta, F. L. Mantia, L. Cui, S. Jeong, H. D. Deshazer, J. W. Choi, S. M. Han, Y. Cui, *Nano Lett.* **2010**, *10*, 708; b) L. B. Hu, J. W. Choi, Y. Yang, S. Jeong, F. La Mantia, L. F. Cui, Y. Cui, *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 21490; c) N. D. Luong, N. Pahimanolis, U. Hippi, J. T. Korhonen, J. Ruokolainen, L. S. Johansson, J. D. Nam, J. Seppala, *J. Mater. Chem.* **2011**, *21*, 13991; d) C. Yan, J. H. Cho, J.-H. Ahn, *Nanoscale* **2012**, *4*, 4870.
[18] a) T. Zhou, C. Zhang, C. B. Han, F. R. Fan, W. Tang, Z. L. Wang, *Acs Appl. Mater. Interfaces* **2014**, *6*, 14695; b) J. Zhong, Y. Zhang, Q. Zhong, Q. Hu, B. Hu, Z. L. Wang, J. Zhou, *ACS Nano* **2014**, *8*, 6273.
[19] C. Zhang, W. Tang, C. Han, F. Fan, Z. L. Wang, *Adv. Mater.* **2014**, *26*, 3580.
[20] W. Tang, C. Zhang, C. B. Han, Z. L. Wang, *Adv. Funct. Mater.* **2014**, *24*, 6684.