

# Ionic liquid-Based High Voltage Flexible Supercapacitor for Integration with Wearable Human Powered Energy Harvesting System

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## Abstract

In this work, we report the fabrication of a high voltage flexible supercapacitor that is able to store energy harvested from a 3D-printed wearable human motion energy harvester and provide power supply to other wearable devices. To bestow the electrode with flexibility, Poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) is incorporated with single walled carbon nanotube (SWCNT) as electrode material, which dramatically decreases its Young's modulus. Furthermore, the supercapacitor is sandwiched between self-healing layers that protects the device from mechanical failure caused by motion when mounted on the human body as wearable device. Owing to the use of ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF<sub>4</sub>), as the electrolyte, the supercapacitor can be charged up to 2.5 V. This wide electrochemical window, with low equivalent series resistance (ESR), enhances the power and energy densities of the supercapacitor to **11 kW kg<sup>-1</sup> and 23 Wh kg<sup>-1</sup>**

The device presents excellent flexibility and mechanical durability. We realized a wearable self-powered and self-sustaining system by the integration of the as-prepared supercapacitor with a 3D-printed mechanical energy harvesting knee brace. Harvested energy generated by a tester wearing the system was sufficient to light up an LED light in a demonstration.

## Keywords

*Supercapacitor, Energy Harvesting, Ionic Liquid, Wearable, Flexible Supercapacitor*

# 1 Introduction

A global booming market of wearable electronics has been predicted since the fast development of the technology of the flexible and wearable devices [1, 2]. Smart sensors, display and communication devices are expected to be integrated together as multifunctional wearable systems which will definitely change our daily lives [3-7]. To create an autonomous functional wearable system, an energy harvesting-storing module is essential to serve as a power supply to other functional system parts [8-10]. Everyone must have experienced the frustration when mobile devices shut down right at the moment when we need them the most. For conventional battery supported devices, adventures end when the batteries are drained. Hence, it is necessary for future portable/wearable devices to contain built-in energy harvesting-storing system, which can dramatically extend the operating time of the device.

Motion energy harvester produces spikes of harvested kinetic energy from time to time in response to “sudden motion” of the users and results in input current surges [11-15]. Within this context, supercapacitors are a promising candidate to buffer the surge and release this energy into the load on demand since they have high power density [16-22]. However, conventional commercial supercapacitors are rigid and inflexible and prone to physical and mechanical damage when they are subjected to practical human motion scenarios such as walking and jogging [23-27]. Hence, to adapt supercapacitors for human energy harvesting, researches on flexible and stretchable supercapacitor devices have attracted much attention [28-40]. Much work on self-powered wearable systems with flexible energy storage have been done, for example, Pu fabricated a self powered textile by stitching a fabric supercapacitor together with a triboelectric energy harvesting fabric [41], Evgenia fabricated a flexible supercapacitor together with a piezoelectric harvester [42] and Wee incorporated a solar cell together with a supercapacitor to obtain a self powered device [43]. Most of these systems, however, are small scale meant for micro systems and seldom pay attention to the robustness of the system.

Besides having flexibility, electronic devices with self-healing property provides an alternative solution to cope with the aforementioned physical and mechanical damage [44-50]. Recently, Chen’s group reported a self-healing supercapacitor, which exhibits excellent mechanical and electrical self-healing behavior [51]. Despite that, the supercapacitors from Chen’s group were

fabricated with aqueous based electrolyte and thus exhibited an electrochemical window within 1 V. This significantly restricts the potential of the device for integration [8, 28].

In this work, we fabricated a high-voltage flexible supercapacitor using ionic liquid gel as electrolyte to improve on the shortcomings of the reported self-healing supercapacitor. Self-healing material composed of supramolecular network and nanoparticles are employed to protect the device from mechanical fracture and failure. Importantly, this is the first demonstration that the as-prepared self healing supercapacitor can be integrated with a mechanical energy harvester. A wearable self-powered and self-sustaining system was subsequently constructed with the integration of the supercapacitor and a 3D-printed energy harvester knee brace. The system is able to harvest human motion energy and keeps an LED light lit up when the tester walks/runs.

## 2 Experimental

### 2.1 Materials

Single-walled carbon nanotube (SWCNT), MnO<sub>2</sub>, Poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF- HFP), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF<sub>4</sub>), chloroform, TiCl<sub>4</sub>, diethylenetriamine, methanol, ethanol, dimethylacetamide (DMAc), 4-methyl-2-pentanone (MP), propylene carbonate (PC) and urea are purchased from Sigma-Aldrich. Pripol 1017 was kindly donated by Croda company.

### 2.2 Fabrication and characterization of ionic liquid-based high-voltage flexible supercapacitor.

The synthesis of self-healing material was performed according to the literature [49], where the dimer acid, Pripol 1017, was condensed with diethylenetriamine and subsequently reacted with urea to form a rubbery self-healing material. TiO<sub>2</sub> was added to the self-healing material to improve its mechanical properties [51]. The electrode and electrolyte were prepared according to the literature with modification: A 50 mL flask was charged with 100 mg of SWCNT, 100 mg of MnO<sub>2</sub>, 240 mg of EMIBF<sub>4</sub> and 160 mg of PVdF(HFP). The contents were then dispersed with 18 mL of DMAc and refluxed at 80 °C for 24 h. Thereafter, the flask was placed in ultrasonic bath for 4 h. The electrode film was obtained by casting 4.8 mL of the resultant gelatinous suspension onto a glass slide (7.5 cm×2.5 cm) and dried at 80 °C for 72 h. The MnO<sub>2</sub> particles have a size of 0.08-

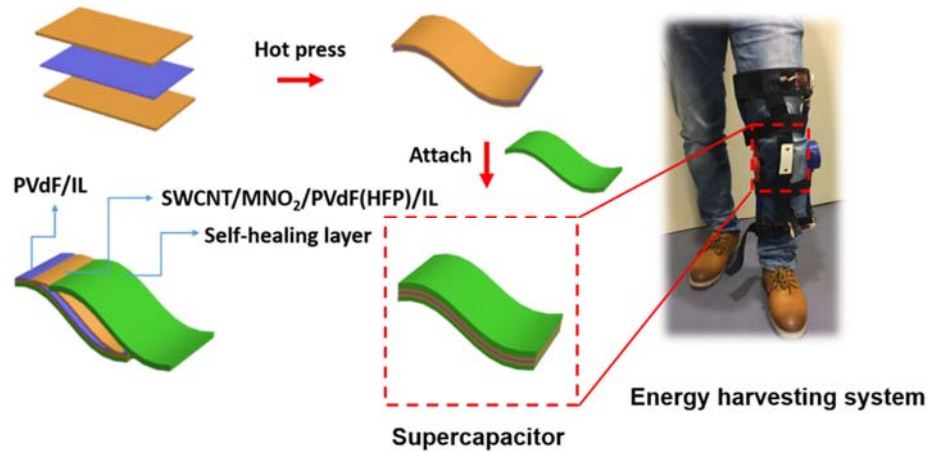
0.1  $\mu\text{m}$  and is found to be uniformly distributed in the electrode film(Figure S.3). To fabricate the electrolyte film, 1.0 g of EMIMBF<sub>4</sub>, 1.0 g of PVdF(HFP), 20 mL of MP and 2.5 g of PC were refluxed at 80 °C for 2 h. 900 $\mu\text{L}$  of the resulting solution were casted onto a glass slide (7.5 cm $\times$ 2.5 cm) and dried at 80 °C for 72 h. The electrode obtained is uniform with a thickness of 80  $\mu\text{m}$  (Figure S2) with sheet resistance measured to be 1.60 ohm sq<sup>1</sup> by 4 point probe testing. The electrolyte film has a thickness of 10-15  $\mu\text{m}$ . Two pieces electrodes film and one piece of electrolyte film used as a separator were assembled by hot-pressing with a weight of 1 kg at a temperature of 80 °C. The thickness of the supercapacitor is about 160  $\mu\text{m}$  after the assembly. Finally, the assembled supercapacitor was sandwiched between two self-healing layers and the fabrication was completed by simply pressing the device with hand.

The device was characterized with cyclic voltammetry, galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) measurements with a potentiostat (Solartron, 1470E with 1455A FRA). Scanning electron microscopy imaging was carried out by field-emission gun scanning electron microscope (JSM-7600F from JEOL, 5 KV). Tensile-stress measurements of as-prepared self-healing composites were carried out by an Instron 5567. The sheet resistance of the SWCNT-MnO<sub>2</sub> electrode was measured by a CMT-SR1000N four-point probe.

### **2.3 Fabrication of human motion energy harvester for supercapacitor integration.**

To demonstrate energy harvesting with the supercapacitor, an energy harvester was printed by 3D printer (Ultimaker 2) using PLA with 100% infill and 0.1mm resolution on a heated bed [52]. The generator is a bipolar stepper motor from OKI model EM-546. The output from the generator is fed into a bridge rectifier IC BAS3007A for rectification and the energy stored in the fabricated supercapacitor. A boost regulator based on the LTC 3105 IC is utilized to maintain a stable voltage to the LED light as the supercapacitor discharges. The voltage measurements were done with a Tektronix TDS1012C-EDU oscilloscope with a 10x probe.

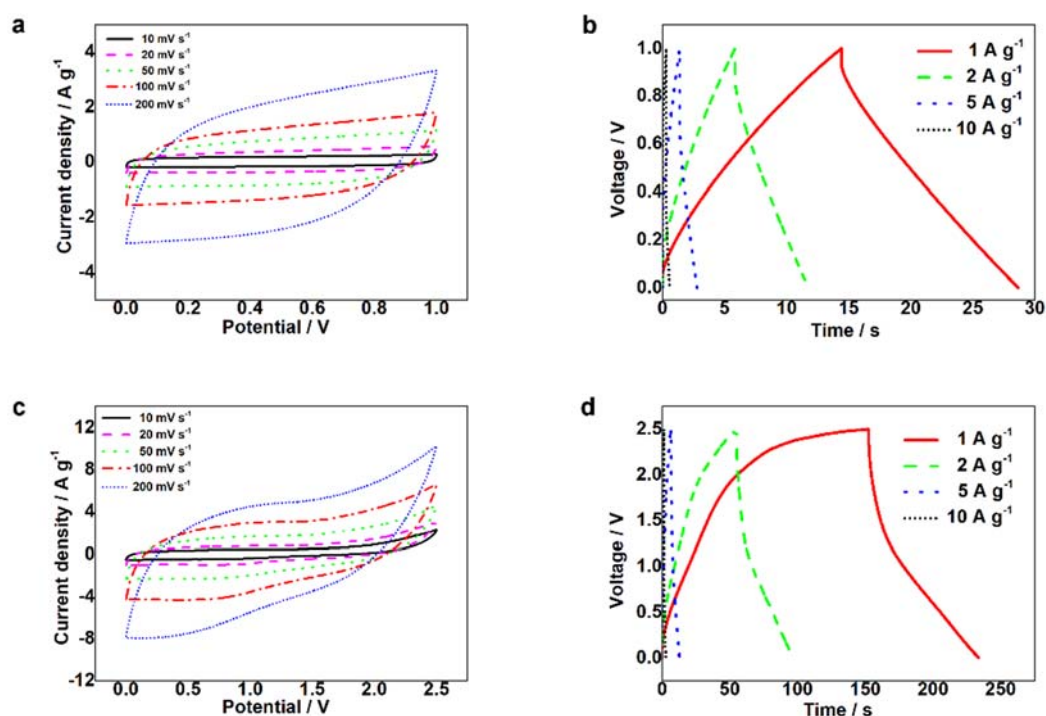
### 3 RESULTS AND DISCUSSION



**Figure 1.** Schematic illustration of the fabrication process of the flexible high voltage supercapacitor and the digital photo image showing the supercapacitor device integrated with the energy harvesting system

The fabrication process of the supercapacitor detailed in the previous section is shown in Figure 1. The electrode and electrolyte separator layers are simply hot pressed together to form the supercapacitor. Self-healing layers consisting of supramolecular network and TiO<sub>2</sub> nanoparticles are then attached to the electrodes, which significantly improved the mechanical property to resist fracture and failure. In the literature, it is common to use SWCNT as binder free electrodes [53] to improve electrolyte accessible surface area and hence enhancing the electrode's specific capacitance. However, due to SWCNT electrode's high stiffness relative to the solid electrolyte, the supercapacitor electrode and electrolyte layers tend to delaminate easily under bending. An addition of PVdF-HFP as a binder into the electrode reduces the electrode's Young's Modulus and improves mechanical matching with the electrolyte layer. The presence of the PVdF-HFP also improves the adhesive strength of the electrode-electrolyte interface by inter-diffusion during heat pressing. The addition of a binder is therefore necessary for a flexible supercapacitor to be durable.

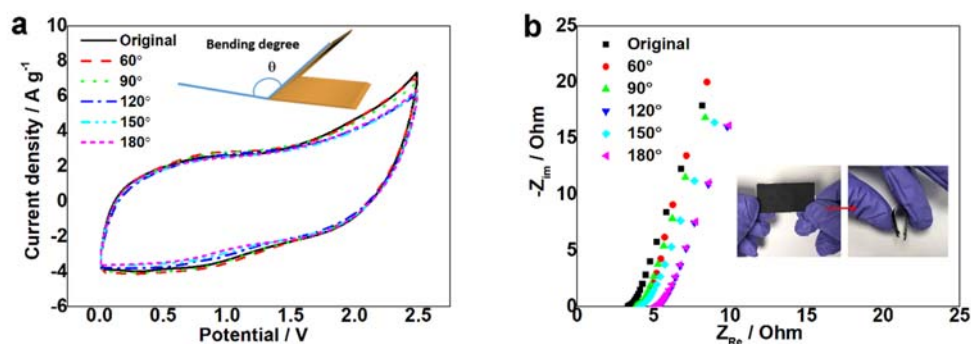
The loss of capacitance due to the addition of a binder from the reduced surface area can be mitigated by the addition of pseudocapacitive materials, like MnO<sub>2</sub>, into the electrodes [54].



**Figure 2.** Cyclic voltammetry and galvanostatic charge-discharge curves of the supercapacitor tested at different potential window.

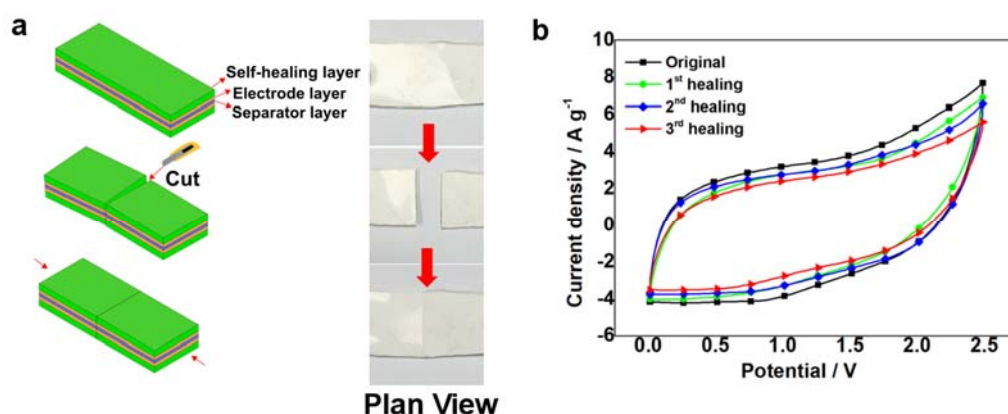
As shown in Figure 2, cyclic voltammetry (CV) and galvanostatic charge–discharge tests were used to investigate the electrochemical properties of the supercapacitors. The CV curves exhibit nearly rectangular shape at a scanning rate from  $10 \text{ mV s}^{-1}$  to  $200 \text{ mV s}^{-1}$  within a potential window of 0-1.0 V (Figure 2a), showing good rate capability. As for the CV curve at the potential window of 0-2.5 V, the shape of the curves deviates from rectangle especially after the voltage reaches 2.0 V. It could be partly due to the lower conductivity and ion mobility in organic gel compared to its aqueous counterpart [55]. Some side reactions might also be involved when the voltage exceeds 2.0 V [55, 56]. However, the capacity of energy storage is still highly enhanced when the supercapacitor is charged to 2.5 V as indicated by the longer discharging time when the device is charged to 2.5 V in comparison with 1.0 V (Figure 2 b,d). When charged to 2.5 V, the specific capacitance, as calculated from the CV curve at  $10 \text{ mV s}^{-1}$  (Figure 2c), is  $110 \text{ F g}^{-1}$ . Using the specific capacitance, the energy density is calculated to be  $23 \text{ Wh kg}^{-1}$  and the power density is  $11 \text{ kW kg}^{-1}$  based on the formula  $V^2/(4RM)$  where  $V$  is the maximum voltage applied,  $R$ , the ESR calculated from the IR voltage drop during charging discharging and  $M$  is the mass of the active material in the supercapacitor [29]. These are much larger values than at lower potential window

of 1V, suggesting the capacity of energy storage is highly enhanced when the supercapacitor is charged to 2.5 V.



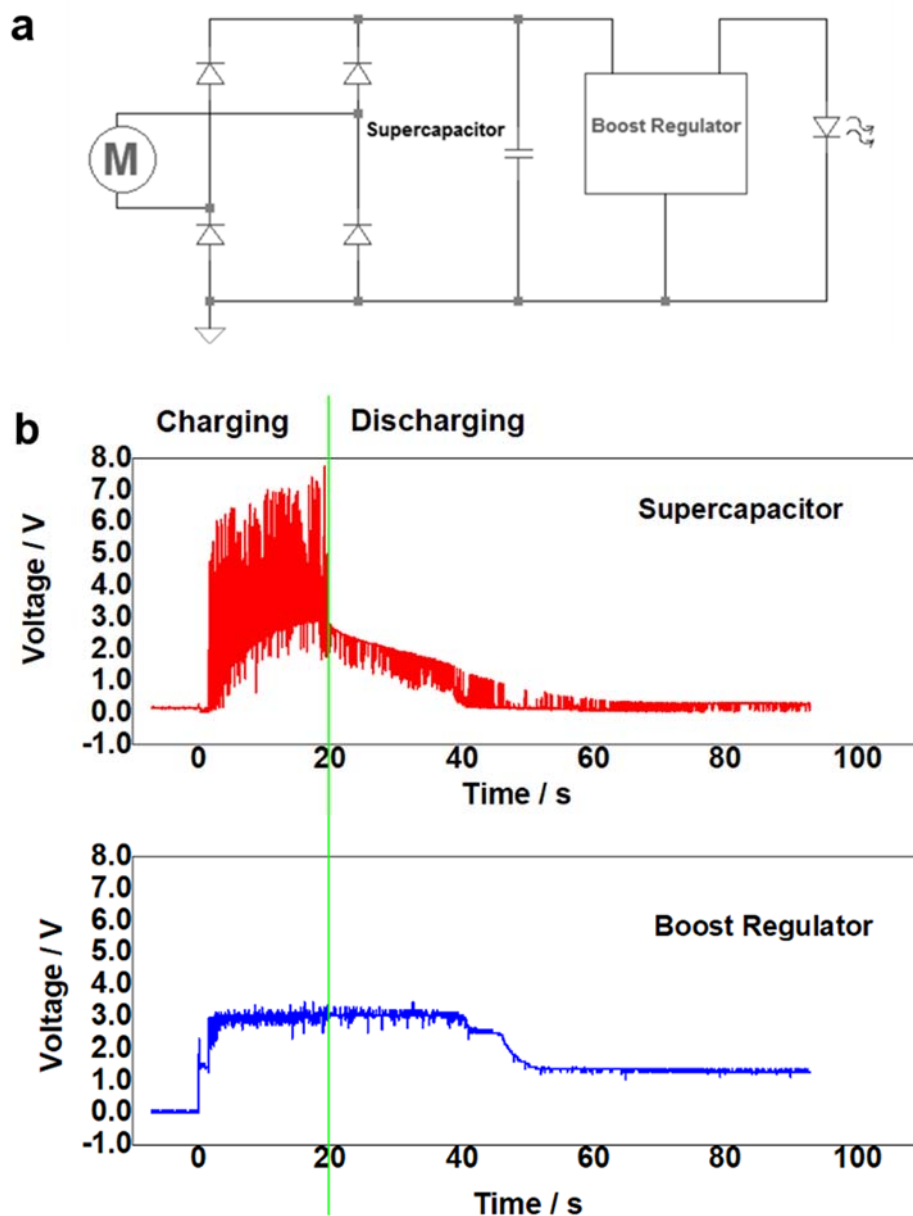
**Figure 3.** Bending test of the supercapacitors. a) Cyclic voltammetry of the supercapacitor bent to different degrees at  $100\text{mVs}^{-1}$ . Inset shows the definition of bending degree. b) Nyquist plots of the impedance change of the supercapacitor bent to different degrees. Inset shows the images of bending process.

Bending tests were carried out to study the flexibility of the device. The evolution of CV curve (Figure 3a) suggests that there were only minor changes in performance when the device was bent gradually to  $180^\circ$  as the curves nearly overlaps with each other. This is in agreement with the impedance measurement of the supercapacitors in Figure 3b. As shown in Figure 3b, the shift of impedance curves suggests that the ESR only slightly increases from  $3.4\ \Omega$  to  $5.2\ \Omega$  during the bending process.



**Figure 4.** Self-healing performance. a) Schematic and optical images of the as-prepared supercapacitor with self-healing layer before cutting (top), after cutting (middle) and after healing (bottom). b) Cyclic voltammetry at  $100\ \text{mV s}^{-1}$  characterization of the supercapacitor during repeated cutting and healing process.

The introduction of self-healing layer into the structure confers the device the capability to prevent failure and survive under extreme conditions. To test the self-healing performance, the supercapacitor was deliberately cut into halves with a pen knife (Figure 4a, middle). The self-healing process was easily initiated by holding the two halves together and applying a gentle pressure for about 10-30 seconds. To probe the performance change, CV curves were monitored during the repeated cutting and healing process (Figure 4b). The supercapacitor maintained functionality after 3 times cutting and healing.



**Figure 5.** Integration of supercapacitor with mechanical energy harvester. a) Illustration of the circuit for integration. b) The supercapacitor was first charged to 2.5 V by hand cranking the energy harvester knee brace and then subjected to discharging using an LED as load. The voltage change of the supercapacitor (upper) and the output of the boost regulator (lower) were monitored via oscilloscope.

Subsequently, we proceeded to the integration of the supercapacitor with mechanical human motion energy harvester. We retrofitted the hinge of a 3D printed knee brace from Thingiverse [52] to become an energy harvester: the hinge was enlarged to house a small electromagnetic generator which was coupled to the rotating motion of the knee brace's hinge through a planetary gear set. The generator produced an alternating voltage output which was passed to a bridge rectifier for rectification (Figure 5a). The rectified voltage was then sent to the supercapacitors and a boost regulator with 3 V output. The circuitry was mounted onto the knee brace to form a complete energy harvesting unit (Figure 1).

As shown in Figure 5b, the supercapacitor (upper) was gradually charged to 2.5 V in 15 s by hand cranking the energy harvesting knee brace. The supercapacitor was then allowed to discharge using an LED as the load. The LED stayed lit as the supercapacitor discharged as indicated by the stable voltage output from the boost regulator (lower). During charging of the supercapacitor, there are numerous transient voltage fluctuations up to 7 V due to the fast cranking of the generator and switching noises in the circuitry. This could have reduced the supercapacitor lifetime and the fluctuations can be reduced by additional low pass filters or clipping circuitry. However, as the voltage spikes last only for a short time and does not affect the operation of the energy harvester within the testing period, we have kept the harvesting circuitry simple for easy integration.



**Figure 6.** Testing of the integration system of supercapacitor and human motion energy harvester. The energy harvester powers the LED and charges the supercapacitor device with energy

harvested from walking (left). After the tester stops walking, the supercapacitor becomes the power source of the LED torch (right).

As a proof-of-concept, the energy harvesting knee brace was tested by a tester wearing the brace and walking on a treadmill. The durability of the supercapacitor was tested by attaching it to a nylon strap and placing the strap in front of the tester's patella. This is to flex the supercapacitor continuously as the tester walks. As seen from the pictures captured from the video (Figure 6, left), the LED light was lit up due to the energy harvested from walking while the supercapacitor was charging at the same time, there was no flickering of the light showing constant, smoothed out voltage supplied by the harvester and the supercapacitor. This accordingly demonstrates the buffering function of the supercapacitors as intended. Despite the constant flexing and shaking from the walk, when the tester stopped walking (Figure 6, right), the light was able to stay lit indicating that the supercapacitor was performing energy storage as expected.

## 4 CONCLUSION

In this work, we fabricated a high voltage flexible supercapacitor, which was proved to be able to integrate with mechanical human motion energy harvester. The supercapacitor was engineered to withstand harsh conditions for real-life applications. The flexible supercapacitor has improved its durability by incorporating PVdF-HFP into the electrode. The electrochemical performance of the supercapacitor was maintained after repeated bending and folding. By using ionic liquid as the electrolyte, the supercapacitor provides a larger voltage output capacity of 2.5 V, thereby enhancing the energy and power densities of the supercapacitor. The as-prepared supercapacitor was successfully integrated with an energy harvester and the supercapacitor served as an energy buffer storage effectively. This is the first report of a facile and successful integration of ionic liquid based high voltage flexible supercapacitor with a human motion energy harvester to power up low-power devices. This opens up the opportunities for further development of the flexible and wearable device for future energy storage and harvesting applications.

**Supporting Information:** Supporting information on the tensile testing, optical image and SEM image of the electrode material is included for this paper.

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