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Flexible self-powered piezo-supercapacitor system for wearable electronics

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KEYWORDS. Single-walled carbon nanotubes; Poly(vinylidene-trifluoroethylene); Piezo-supercapacitor; Energy harvesting; Energy storage

ABSTRACT

The integration of the energy harvesting and energy storage in a single device both enables the conversion of the ambient energy into electricity and provides a sustainable power source for various electronic devices and systems. On the other hand, mechanical flexibility coupled with optical transparency of the energy storage devices is required for many applications, ranging from self-powered rolled-up displays to wearable optoelectronic devices. We integrate a piezoelectric poly(vinylidene-trifluoroethylene) film into a flexible supercapacitor system to harvest and store the energy. The asymmetric output characteristics of the piezoelectric P(VDF-TrFE) film under mechanical impacts results in the effective charging of the supercapacitors. The integrated piezo-supercapacitor exhibits a specific capacitance of 50 F g^{-1} . An open circuit voltage of the flexible and transparent supercapacitor reached 500 mV within 20 s during the mechanical action. Our hybridized energy harvesting and storage device can be further extended for providing sustainable power source of various types of sensors integrated into wearable units.

INTRODUCTION

Energy harvesting is essential to achieve independent and sustainable electronic devices, needed in self-powered systems, where no batteries are required, for environmental monitoring and sensing or for biomedical devices in wearable electronic applications.¹⁻⁴ Taking forms of irregular air flow/vibration, ultrasonic waves, body movement, and hydraulic pressure, mechanical energy is ubiquitously available in our living environment.⁵ For the past decades, energy harvesting from the environment has created a huge impact on the energy sector and thus the scientific community.³ Therefore, devices, which convert low-frequency vibration and environmental activities (e.g., wind, sound, friction, motion, and thermal energy) into electrical energy through piezoelectric, triboelectric or pyroelectric effects have been implemented.⁶ The harvested energy is sufficient for the operation of small electronic devices in an aperiodic manner using energy storage devices. However, real time generators are required to have effective electrical output and longer cycle stability to support continuous operation in environmental monitoring, defense, and implantable biomedical device applications. Moreover, if such systems are realized in an advanced form, such as flexible, transparent and lightweight, they will immediately become solutions for wearable consumer electronics, serving as both energy harvesters and charging components. Many research groups have attempted to fabricate high performance energy harvesters using different materials and form-factors (e.g., films, fibers, and composites).²⁻¹²

Piezoelectric materials can convert ubiquitously irregular and low frequency mechanical vibration into electricity and have been extensively studied for the use of energy generators. Piezoelectric fluoropolymers, such as polyvinylidene fluoride (PVDF) and its copolymer poly(vinylidene-trifluoroethylene) (P(VDF-TrFE)), on the other hand, are lightweight, spinnable, soft, and flexible, making them excellent potential candidates for the functional wearable electronics applications.¹³⁻¹⁵

New technologies that can harvest energy from the environment as sustainable self-sufficient micro/nano-power sources offer a possible solution. Potential energy sources are solar, wind, thermal electric, biomass, chemical, and mechanical. Comparing with other types of energy harvesting, mechanical energy is nearly independent on weather and working environment. Moreover, the mechanical energy available in our environment has a wide spectrum of frequencies and time-dependent amplitudes.

In this work, we propose to combine and to utilize energy harvesting and storage devices in a flexible manner, with the connection of piezo-harvester and energy storage device as two separate portable and easily dismountable units, without the use of any complicated liquid processes of the system fabrication. Our system consists of solid-state supercapacitor

based on single-walled carbon nanotube (SWCNTs) films electrodes and P(VDF-TrFE) metalized film as energy harvester. The transparent and flexible supercapacitors exhibited the self-charging capability under repeatable applied force and can be charged up to 500 mV in 20 s. At the same time, the maximum voltage generated by fabricated the hybrid piezo-supercapacitor system reached about 650 mV. Thereby, we demonstrate a simple approach for creation of self-powered piezo-supercapacitor based system, which can find its novel applications in wearable electronics.

EXPERIMENTAL

Materials and characterization

The SWCNT were synthesized by an aerosol chemical vapour deposition (CVD) method described elsewhere.^{16,17} Briefly, a vapour of catalyst precursor, ferrocene, is supplied into the CVD reactor, where it decomposes in the atmosphere of carbon monoxide, forms nanometer-sized catalyst particles on the surface of which carbon monoxide (CO) disproportionation occurs and finally SWCNTs grow. The flow at the outlet of the reactor is filtered and SWCNTs are collected onto the nitrocellulose filter. Simply, by varying the duration of the collection time one could obtain the films of different thickness and transparency. Importantly, the SWCNT films could be easily transferred to different substrates by dry-deposition technique,^{18,19} such as polyethylene terephthalate (PET), used in this work.

The films form a randomly oriented network of SWCNTs as can be seen from SEM image in Fig. 1(a). TEM observation confirmed that the produced tubes are single-walled carbon nanotubes (Fig. 1(b)) that makes them ideal for supercapacitors electrode. In order to further investigate the structure of the SWCNT film we characterized them using Raman spectroscopy (Fig. 1(c)). Typical Raman peaks for SWCNTs are present: RBM (radial breathing mode), associated with vibration of carbon atoms in a radial direction; G-band around 1580 cm^{-1} is indicative of a graphitic structure, while D-band around 1350 cm^{-1} corresponds to disordered carbon and 2D band, the result of two phonon lattice vibrational process. High intensity ratio between G and D bands (1:35) shows that the SWCNTs are of high quality that determines unique mechanical and electrical properties.

Fig. 1. Characterization of single-walled carbon nanotube films: (a) SEM image of SWCNT films used as electrodes of the flexible supercapacitor. (b) TEM image of CNTs, confirming that the films consist of SWCNTs. (c) Raman spectrum of SWCNT film.

For piezoelectric polymer preparation P(VDF-TrFE) copolymer powder (Piezotech) with trifluoroethylene (TrFE) content of about 30% was used. P(VDF-TrFE) powder was dissolved in dimethylsulfoxide/acetone (DMSO/Ac) solution followed by casting of the films from the solutions. Process of crystallization was performed during two-three hours at the temperature of 100°C until complete evaporation of the solvents. As the film thickness affects the generation efficiency, several thicknesses were tested (Fig. S1(a) and S1(b)). Samples with chosen thicknesses of 40 μm and rectangular shape of 7x4 cm^2 were prepared. Thicknesses of the fabricated samples were measured by Thickness gauge device Mitutoyo 1-34521. P(VDF-TrFE) samples were polarized in external electrical field of 20 kV cm^{-1} . In order to measure P(VDF-TrFE) film response, metallic aluminium electrodes were deposited by magnetron sputtering, on both sides of the film. The thickness of the metal electrodes was 100 nm on each side of the piezo film.

The morphology and structure of SWCNT films was investigated using scanning electron microscope (FEI Helios Nanolab 660) and transmission electron (Tecnai G2). Raman spectrometer Horiba Jobin-Yvon Labram HR with a 633 nm laser was used to investigate the purity of the SWCNT films. The open circuit output voltage response of piezoelectric materials was measured using an oscilloscope (Tektronix MDO3102). Cyclic voltammetry and galvanostatic charging–discharging were carried out using an electrochemical workstation (Elins Potentiostat-galvanostat P-40X). The resulting voltage obtained by the piezo-supercapacitor system was measured by Keysight 34410A and Keithley 2400 source meters.

Fabrication of flexible supercapacitor

For the flexible prototypes PET substrates with the thickness of 80 μ m was utilized. A piece of the PET film was cleaned with ethanol using an ultrasonic cleaner and was then used as the substrate material of the supercapacitor. PET films were cut into pieces of rectangular shape with the size of 2x2 cm², followed by dry transferring of the SWCNT films on top as both electrodes and current collectors. Before the deposition, SWCNT films were heated on a filter to 200°C for a surface annealing. This step was found to be essential for desorption of oxygen and removing organic impurities from the surface of the SWCNTs.

A gel containing polyvinyl alcohol (PVA) powder (5g) and H₂SO₄ (5g) in water (50 mL) was used as the solid gel-electrolyte. After mixing the compounds, viscous solutions were cast onto the SWCNT electrodes, subsequently two electrodes were coated with gel electrolyte and dried in the air at room temperature for 10 h, in order to PVA/H₂SO₄ gel-electrolyte essentially become uniform layer with the thickness of around 100 μ m. After drying two similar electrodes were pressed together and glued during the process of PVA/H₂SO₄ gel solidification.²⁰

Fabrication of self-powered piezo-supercapacitor system

The whole piezo-supercapacitor system was assembled in one unit through the rectifying diode-bridge connection. Flexible supercapacitor was fixed on top of the specially designed motorized setup for repeatable mechanical action and connected to the metalized piezo-film, which was fixed inside of the motorized setup frame. Two electrodes of the supercapacitor were connected to the source meter for the measurements of charging processes, occurred during mechanical action of the whole system.

RESULTS AND DISCUSSION

Fig. 2(a) shows the schematic process flow of the fabrication of the flexible piezo-supercapacitor. We used SWCNT films as the supercapacitor electrode because its excellent mechanical stability and flexibility allow it to withstand intense mechanical deformation and vibration while at the same time being highly conductive. The structure of the SWCNTs can be described as a randomly oriented network, which makes the SWCNT film a promising candidate for electrode material due to high connectivity resulting in high specific surface area (950 m² g⁻¹)²² and highly conductive surface area readily accessible for an ion absorption.

Moreover, this kind of SWCNT network structure allows flexing the electrode so that connections between the SWCNTs remain stable during mechanical actions.

Fig. 2(b) shows cross-sectional optical image of the supercapacitor structure, which shows that SWCNTs are fully immersed into the PVA/H₂SO₄ electrolyte, glued between two PET substrates. The whole thickness of the flexible supercapacitor is around 250 μm . Fig. 2(c) is a photograph of the planar flexible supercapacitor in the relaxed state, where the transparency of the device can be observed, and in flexed state (Fig. 2(d)).

Fig. 2. (a) Schematic illustration of the flexible supercapacitor fabrication: SWCNT film/PET electrodes are coated with PVA/H₂SO₄ electrolyte and assembled together; (b) cross section of the supercapacitor, which consist of symmetric SWCNT film/PET electrodes and PVA/H₂SO₄ electrolyte. Photographs of the flexible and transparent supercapacitor in relaxed (c) and flexed states (d).

After viscous PVA/H₂SO₄ gel deposited on two SWCNT film/PET electrodes was solidified, cyclic voltammograms (CVs) characteristics were measured by the potentiostatic procedures at different scan rates from 100 to 1000 mV s^{-1} . Fig. 3(a) shows a typical charging process of the supercapacitor. The current increased with the increasing scan rate, as it is characteristic for adsorption-controlled reactions, implying that no mass transfer or kinetic limitations can be observed and all the SWCNT surface sites are readily accessible even with the higher scan rates. Thus, the same capacitance is achieved in the studied scan rate range. Fig. 3(b) shows the triangle shaped galvanostatic charging-discharging (GCD) curve of the

flexible supercapacitor, which were conducted at 0.25 A g^{-1} (3.25 mA m^{-2}) current value, demonstrating the reversible capacitive behavior.

Fig. 3. Electrochemical performance of the supercapacitors device with PVA/H₂SO₄ gel electrolyte: (a) cyclic voltammograms of flexible prototype measured at scan rates of 100, 200, 500 and 1000 mV s⁻¹. (b) Galvanostatic charge and discharge curve measured at current of 0.25 A g⁻¹ (3.25 mA m^{-2}).

The specific capacitance of this device (C_{sp}) can be calculated using charge integrated from the area of the cyclic voltammogram graphs according to the equation (1)²¹:

$$C_{sp} = \frac{1}{2m\nu} \int_{V_-}^{V_+} I(V)dV, \quad (1)$$

where ΔV is a voltage range between the electrodes, m is a mass of the active material in a single electrode (g), ν is a scan rate (mV s⁻¹). The mass density of the used SWCNT films is $5.1 \mu\text{g cm}^{-2}$.²² The specific capacitance of flexible supercapacitor, based on PET/SWCNT electrodes, was calculated to be around 50 F g^{-1} .

Before charging the flexible supercapacitor, the initial voltage of the device was discharged to zero. After that, the charging process was performed across the piezo-electric P(VDF-TrFE) under external mechanical action by generated voltage potential. The P(VDF-TrFE) film in our system serves as the piezoelectric energy harvester, which can convert mechanical vibration into electricity.²³ This potential, generated by P(VDF-TrFE), can drive the ions in the electrolyte of the supercapacitor to migrate towards the interface within the symmetric SWCNTs electrodes, establishing a pseudo-capacitance at the interface and storing the electricity in the form of electrochemical energy.

To measure the potential difference obtained on piezo-generator coated with thin metal layers the system was assembled as it is shown in Fig. 4(a). P(VDF-TrFE) metalized film was used as

piezoelectric generator to harvest energy when beat back and forth by a “motorized hand” at a frequency of 2.5 Hz. Fig. 4(b) and 4(c) are photographs of the setup with the flexible and transparent supercapacitor connected through the diode-bridge to the P(VDF-TrFE) film, fixed in the frame. Red arrows in Fig. 4(b), (c) shows the direction of the “motorized hand” movement: when the deflection angle reaches 30°, frame goes back to the horizontal position while striking the table. Fig. 4(d) shows the output voltage profiles of the P(VDF-TrFE) film with two opposite polarity peaks under a periodic mechanical action. The positive peak corresponds to the stage under compressive force, while the negative peak represents the natural relaxation process. The similar duration of the two stages gives rise to the symmetric characteristics of the amplitude in the two peaks, which dictates the need in charging of the supercapacitor with a rectification unit. Storing the generated energy and driving functional electronic devices require a regulated DC power supply while piezoelectric harvesters generate time-varying voltages; therefore, the rectification is essential. After integration of diode-bridge to the system, the open-circuit voltage generated by the piezo film was measured again. Fig. 4(f) demonstrates repeatable voltage peaks up to 2 V with the same positive polarity, which enables domination of the supercapacitor charging process. For the proper characterization of piezo harvester along with open-circuit voltage short-circuit current is measured. It is observed that piezo-film shows current output close to 300 nA, which is in a good agreement with the previously reported values for such materials (Fig. 4 (e)).²⁴

Fig. 4. (a) Schematic image of the built piezo-supercapacitor system and (b)-(c) its photographs during the mechanical action testing by a “motorized hand”. (d) The open-circuit voltage of as-assembled P(VDF-TrFE) film before rectification and (e) its short-circuit current. (f) The open-circuit voltage of the piezo-film after the diode-bridge integration.

To measure the voltage generated by the system with the load and driven by mechanical actions, different load resistors were connected in parallel with the supercapacitor (Fig. 2(a)). As shown in Fig. 2 (b), when resistance is high, the power consumption with the load is lower than the power provided by the system without it. As the load resistance decreases, the power consumption increases and the charging voltage slope decreases.

To confirm that the increased voltage of the supercapacitor is a result of the piezoelectric generator, we measured the voltage response of the flexible prototype under the same periodic force conditions. We calculated the average mechanical force applied to the piezoelectric layer during the mechanical action to be about 12.2 N. This value can be commonly obtained by a human hand and considered as a driving force for operation of the device without the use of motorized setup. Figs. 5(a) and (b) show a typical charging process of the whole device, working as flexible piezo supercapacitor system. At first, the initial voltage of the devices was discharged to zero. After that, the charging process was performed under a periodic force of “motorized hand”, with the same frequency of 2.5 Hz. Then, the devices were discharged again. According to measured voltage of the flexible supercapacitor, it increased up to 500 mV within 20 s after several repeated beating processes. Based on the obtained values we have calculated the energy density of our system to be 5.06 W h g^{-1} at a power density - 182.25 W g^{-1} . Moreover, in order to measure the maximum voltage, which can be generated for such type of supercapacitors by piezo-film we measure it during continuous beating process for 100 seconds. As it is shown in Fig. 5(b) the maximum voltage generated by fabricated piezo-supercapacitor system reached about 650 mV with slight decrease to 600 mV by 100 second.

Fig. 5. Self-charging performance of piezo-supercapacitor system (a) after several beating cycles and (b) after continuous beating, demonstrating saturated state of the device.

P(VDF-TrFE) is widely investigated due to its excellent mechanical flexibility and high piezoelectric constant. Due to this fact, such material as P(VDF-TrFE) has been already used as a piezo-generator for self-charging power cells. However, voltage response in these works reached up to 300 mV within 240 s,²⁵ 100 mV for 40 s,²⁶ 110 mV for 300 s,²⁷ which is at least six times lower and five times slower than the results, obtained in our work. However, for driving LEDs backlights or powering analog circuits and other small electronic devices it requires low leakage currents and voltages that are higher than the input supply voltage. We propose several strategies to overcome these problems. In order to reduce the leakage current and increase the self-discharging time of the supercapacitor, used in our system, one can reduce the capacitance losses by choice of electrodes and therefore interface of the electrode/electrolyte. As SWCNTs are ideal candidates for flexible device electrodes, they can be modified by various coatings in order to form SWCNTs/oxide and SWCNTs/polymer composite films to enhance the capacitance and stability of the device. Moreover, the increase of the input voltage can be achieved by integration of tandem device structure, which would consist of sandwiched piezo-films and several supercapacitors connected in parallel; or by the use of step-up DC/DC converter and improved power management design, as it was successfully demonstrated by Niu *et. al.*²⁸

CONCLUSIONS

In summary, we have successfully demonstrated the technology of flexible piezoelectric-driven self-charging supercapacitor power cell fabrication, which is based on P(VDF-TrFE) metalized piezo-film and transparent supercapacitor with SWCNT film/PET electrodes and PVA/H₂SO₄ electrolyte, which can be used to simultaneously harvest and store the mechanical energy to electrochemical energy. A polarized P(VDF-TrFE) metalized film was fixed in a special “motorized hand” and external mechanical impact establishes a piezoelectric potential across this film, while the whole system produces the mechanical action at a frequency of 2.5 Hz. Piezoelectric film serves as a driving force for flexible supercapacitor charging and therefore storing the energy in the form of electrochemical one. The supercapacitors exhibited the self-charging capability under repeatable applied force and can be charged up to 500 mV in 20 s. At the same time, the maximum voltage generated by fabricated piezo-supercapacitor system reached about 650 mV. The fabrication procedure is simple and could be easily scaled-up to large-scale production. The piezo-supercapacitor system provides a new promising direction in the supercapacitor research for

the development of next generation self-powered sustainable power sources for wearable and flexible electronic devices.

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SUPPLEMENTARY INFORMATION

Flexible self-powered piezo-supercapacitor system for wearable electronics

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Figure S1. Voltage generated in P(VDF-TrFE) film with different thicknesses: 20 μm – (a), 40 μm – (b).

Figure S2. (a) Circuit diagram of the system with different load resistances (470 k Ω , 680 k Ω and 1 M Ω). (b) Time dependence of the voltage stored by the system with the use of different load resistances.