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All-Plastic-Materials Based Self-Charging Power System Composed of Triboelectric Nanogenerators and Supercapacitors

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Triboelectric nanogenerators (TENG) are a possible power source for wearable electronics, but the conventional electrode materials for TENG are metals such as Cu and Al that are easy to be oxidized or corroded in some harsh environments. In this paper, metal electrode material is replaced by an electrical conducting polymer, polypyrrole (PPy), for the first time. Moreover, by utilizing PPy with micro/nanostructured surface as the triboelectric layer, the charge density generated is significantly improved, more superior to that of TENG with metals as the triboelectric layer. As this polymer-based TENG is further integrated with PPy-based supercapacitors, an all-plastic-materials based self-charging power system is built to provide sustainable power with excellent long cycling life. Since the environmental friendly materials are adopted and the facile electrochemical deposition technique is applied, the new self-charging power system can be a practical and low cost power solution for many applications.

1. Introduction

The energy crisis and environmental issues have cast a huge shadow upon human modern life, which have impelled extensive research in renewable energy, such as solar energy, hydro and wind power.[1] Nanogenerators, a novel clean and sustainable power provider that can harvest energy from environment in our daily life, have drawn much attention recently.[2–8] The triboelectric nanogenerators (TENG) utilizes the most common materials to convert almost all forms of mechanical energy into electricity including pressing, vibrations, airflow, rain drops, water wave, rotations, etc.[9–22] Based on the coupling between triboelectric effect and electrostatic induction without using magnets and metal coils, TENG has many advantages including flexibility, light weight, and small size.

Currently, the electrode materials of TENG are metals such as Cu or Al fabricated by physical vapor deposition,[23–28] which are easily oxidized or corroded in some harsh environments.[29] Alternatively, electrically conducting polymers (ECP) can serve as materials for electrodes and triboelectric layers that can be easily prepared by electrochemical deposition techniques. ECP are high electrical conductive and stable, and the electrochemical deposition method is facile and has excellent controllability in film morphology and electrically conducting behavior.

Since TENG gives pulsed output power that cannot be directly utilized by conventional electronics, an energy storage component is essential for the practical applications of TENG.[30,31] Among the state-of-art energy storage techniques, electrochemical capacitors, also known as supercapacitors, have been characterized with high power density, long cycling life, environmental benignancy, etc.[32–36] which makes them a good match for TENG. Especially, long cycling life is a desirable factor for those devices that require sustainable and maintenance-free power source, such as sensors and power generating networks that are wildly distributed in a vast area.

Features of supercapacitors are largely decided by their electrode active materials. Among them, conducting polypyrrole (PPy), due to its high electric conductivity and specific capacitance, good chemical and thermal stability, facile synthesis, low cost, environmental friendly, and biocompatible,[37] had been considered as one of the most promising electrode materials.[38,39] Moreover, since PPy films can be in situ prepared on electrodes as self-supporting films without binder, their mechanical strength is much better than that of commercial carbon-based electrodes. These features of PPy make it a perfect material to be used in TENG as triggered by mechanical motions.

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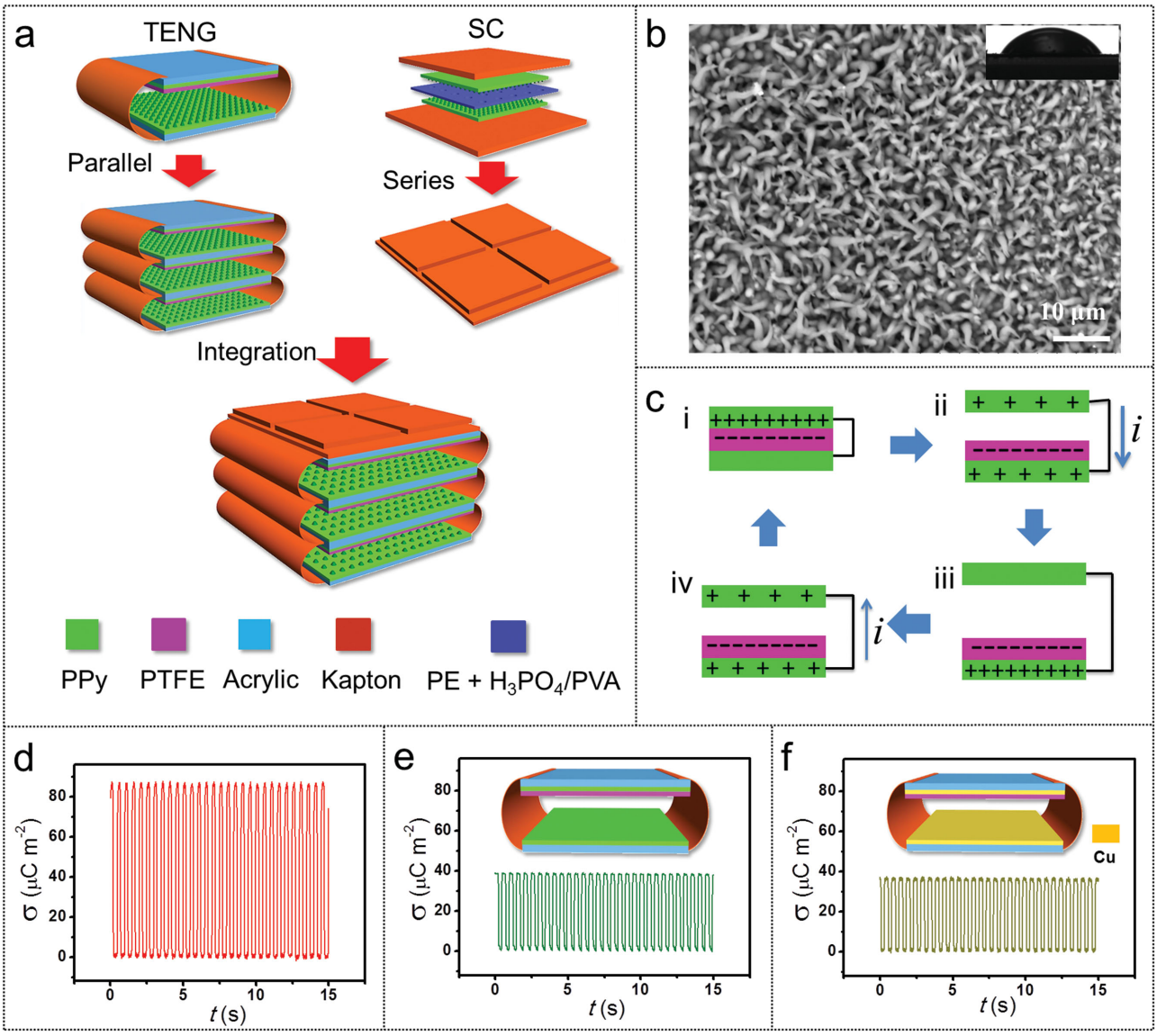

Figure 1. Overview of the all-plastic-materials based self-charging power system. a) Schedule of the integrated self-charging power system from 3-parallel TENG and 4-series supercapacitors (SC). b) SEM image of hPPy, which is used as triboelectric electrode of TENG and electrode active material of supercapacitors, with its water-contacting angle shown in the up-right corner. c) Brief mechanism of the TENG. d) Triboelectric surface charge density of the TENG with hPPy as triboelectric electrode and cPPy as back electrode. e) Charge density of the TENG with cPPy as both triboelectric electrode and back electrode, inset shows the structure of cPPy-based TENG. f) Charge density of the TENG using copper as both triboelectric electrode and back electrode, inset shows the structure of Cu-based TENG.

In this work, new TENG are fabricated with PPy as its triboelectric layer and electrode material instead of metals for the first time. They are then assembled with PPy-based supercapacitors to build an all-plastic-materials based self-charging power system, which can directly power various electronic devices and be anticorrosion at even harsh ambient environment.[29] All components of this system are plastic, including electrodes and dielectric of TENG, active materials and electrolyte of supercapacitors as well as the substrates and spacer. Especially, a micro/nanostructured PPy with novel hollow horn-like morphology (hPPy) is applied as the triboelectric layer and this hPPy-based TENG gives twice power as that of TENG using metal or conventional cauliflower-like PPy (cPPy) as the triboelectric layer, which reveals a huge potential of hPPy as triboelectric layers and electrodes for TENG.

2. Results and Discussion

As illustrated in **Figure 1**a, the all-plastic-materials based self-charging power system is fabricated by integrating PPy-based TENG and supercapacitors. In TENG, polytetrafluoroethylene (PTFE) is used as a triboelectric layer with cPPy as the back electrode and hPPy as the other triboelectric layer and

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electrode at the same time, as called the triboelectric electrode. To improve the output charge and current, several TENG (typically three) are stacked together and connected in parallel. In supercapacitors, hPPy is applied as the electrode active material of both anode and cathode, while porous polyethylene (PE) film and H_3PO_4/PVA (polyvinyl alcohol) gel are adopted as separator and electrolyte. In order to improve its output voltage, four supercapacitors are connected in a series. A typical morphology of cPPy is shown in Figure S1 (Supporting Information), showing relatively smooth in the surface morphology; while in the case of hPPy (Figure 1b), the micro/nanostructure horns grow on its surface to form dense and homogeneous arrays, with an average diameter of about 100 nm, length of 5–10 μm and approximate micro/nanohorns density as 10^6–10^7 per cm^2. This morphology configuration is well controlled by several tunable parameters of the electrochemical pulse deposition technique, such as polymerization potential and pulse period as reported previously.[40] The unique micro/nanostructure on the surface of hPPy can enlarge the effective contact area and hence enhance the contact electrification for TENG. Given the hydrophilic property of hPPy, as its water-contacting angle is 62° (the up-right corner of Figure 1b), the high specific surface area arisen from the micro/nanostructure of hPPy can greatly improve the electrochemical capacitance performance for supercapacitors.

Figure 1c shows the mechanism of TENG under vertical contact-separation mode, which is a coupling between triboelectric effect and electrostatic induction. When the triboelectric electrode, namely the hPPy film, contacts the PTFE film, electrons on the hPPy surface transfer to the surface of PTFE (i). Once the hPPy leaves, positive charges are induced on the back electrode, i.e., the cPPy film (ii); then electrons flow from the cPPy film to the hPPy film and finally reach a balance (iii). As the hPPy film approaches the PTFE film, the induced positive charges on the cPPy films are reduced, and then electrons flow back from the hPPy to the cPPy film (iv) and ultimately reach a new balance, until the hPPy contacts the PTFE film again (i).

From our previous study, the triboelectric surface charge density (σ) is the most important parameter since the performance figure-of-merit (FOM) of a TENG is proportional to square of it.[15] Therefore, we compare the triboelectric surface charge density produced by TENG using hPPy, cPPy and Cu as triboelectric electrode, respectively, as shown in Figure 1d–f. The charge density of hPPy-based TENG is up to 84 μC m^{-2}, which is far more superior to that of the other two. Even cPPy-based TENG makes equal charge density as Cu-based one does, which enables all-plastic materials to replace the conventional metal electrode for TENG. Here, the key improvement of charge density and hence the performance is resulted from two aspects: first, the micro/nanostructure of electrode material that enlarges the effective contact area; second, the micro/nanostructure of hPPy is much more shape-adaptive during contact (similar to the behaviors of liquid metals), which leads to a high contact-intimacy for more efficient triboelectrification.[15,41] These findings uncover a great potential in material choice and surface modification of triboelectric electrode in optimizing the output performance of TENG.

The high charge density of hPPy-based TENG is constant while the contacting frequency (f) increases (**Figure 2**a). Its perfect cycling stability throughout three million cycles is revealed in Figure 2b, before and after which the charge density remains the same. The peaks value of short-circuit current (I_{SC}) keeps rising with the increase of contacting frequency, from 7 mA m^{-2} at 2 Hz to 30 mA m^{-2} at 10 Hz, while its open-circuit voltage (V_{OC}) remains steady as around 48 V (Figure S2a,b, Supporting Information).

The three stacked hPPy-based TENG were connected in parallel to improve the output charge and current. Compared to the single hPPy-based TENG, the triboelectric surface charge of 3-parallel TENG is enhanced from 26 to 74 nC and the peak of short-circuit current is from 8 to 26 μA (Figure S3a,b, Supporting Information). Its charge density is 82 μC m^{-2} and the peak value of I_{SC} increases from 6 mA m^{-2} at 2 Hz to 28 mA m^{-2} at 10 Hz (Figure 2c,d). Its V_{OC} at various frequencies is around 28 V (Figure 2e), which is lower than that of the single TENG because the average maximum gap between the triboelectric electrode and dielectric layer achieved in 3-parallel TENG is smaller than that of the single one. Figure 2f presents a proper load of 100 MΩ to 1 GΩ that gives the maximum output power of ≈5.5 W m^{-2}. Although each triboelectric area is as small as 1.7 cm × 1.7 cm, the 3-parallel TENG are still able to light up 32 light-emitting diodes (LEDs) only by manual pressing them (Figure 2f and Video S1, Supporting Information), which demonstrates it as an efficient energy harvester.

Performance analysis of a single hPPy-based supercapacitor is illustrated in Figure S4 (Supporting Information) and **Figure 3**a,b. The imaginary part of impedance (Z_{Im}) is almost vertical to the real part (Z_{Re}) in electrochemical impedance spectroscopy (EIS) curve (Figure S4a, Supporting Information), indicating an ideal capacitive behavior. A stable high capacitance plateau exists in low frequencies area (the up-right corner of Figure S4a, Supporting Information), 7.4 mF at 10 mHz according to Equation S1 (Supporting Information), signifying fast charging/discharging ability. Rectangle-like cyclic voltammetry (CV) curves at a scanning rate of 50 and 100 mV s^{-1}, suggest its very fast electrochemical switch ability (Figure S4b, Supporting Information). Generally, the pseudocapacitive nature of PPy leads to peaks in CV curves. However, as reported by Conway et. al, rectangle-like CV curves with no peak will present when the pseudocapacitive electrode has very fast charging/discharging ability, which is just the case for hPPy.[39,42] The voltage (V) is linear in the entire window (0–0.7 V) with no obvious ohm-drop phenomenon in galvanostatical charging/discharging (GCD) analysis at a current load (i) of 50 and 100 μA (Figure 3a). The discharging capacitance calculated here is 7.8 mF (Equation S2, Supporting Information), indicating an energy density of 98 J g^{-1}. The capacitance from GCD is slightly higher than that from EIS data due to the redox switch hysteresis of conducting polymer.[43] Its good stability is validated by a 10,000 cycling test, where its GCD patterns remain nearly identical (Figure 3b).

To improve output voltage of the power system, four hPPy-based supercapacitors are connected in series and a voltage window of 0–2.5 V is obtained (Figure 3c). The rectangle-like CV curves, where each response current had been divided by its scanning rate, have similar area from 10 to 100 mV s^{-1}. This fast charging ability enables it to response the pulse output of TENG swiftly. Similar impedance and voltage properties

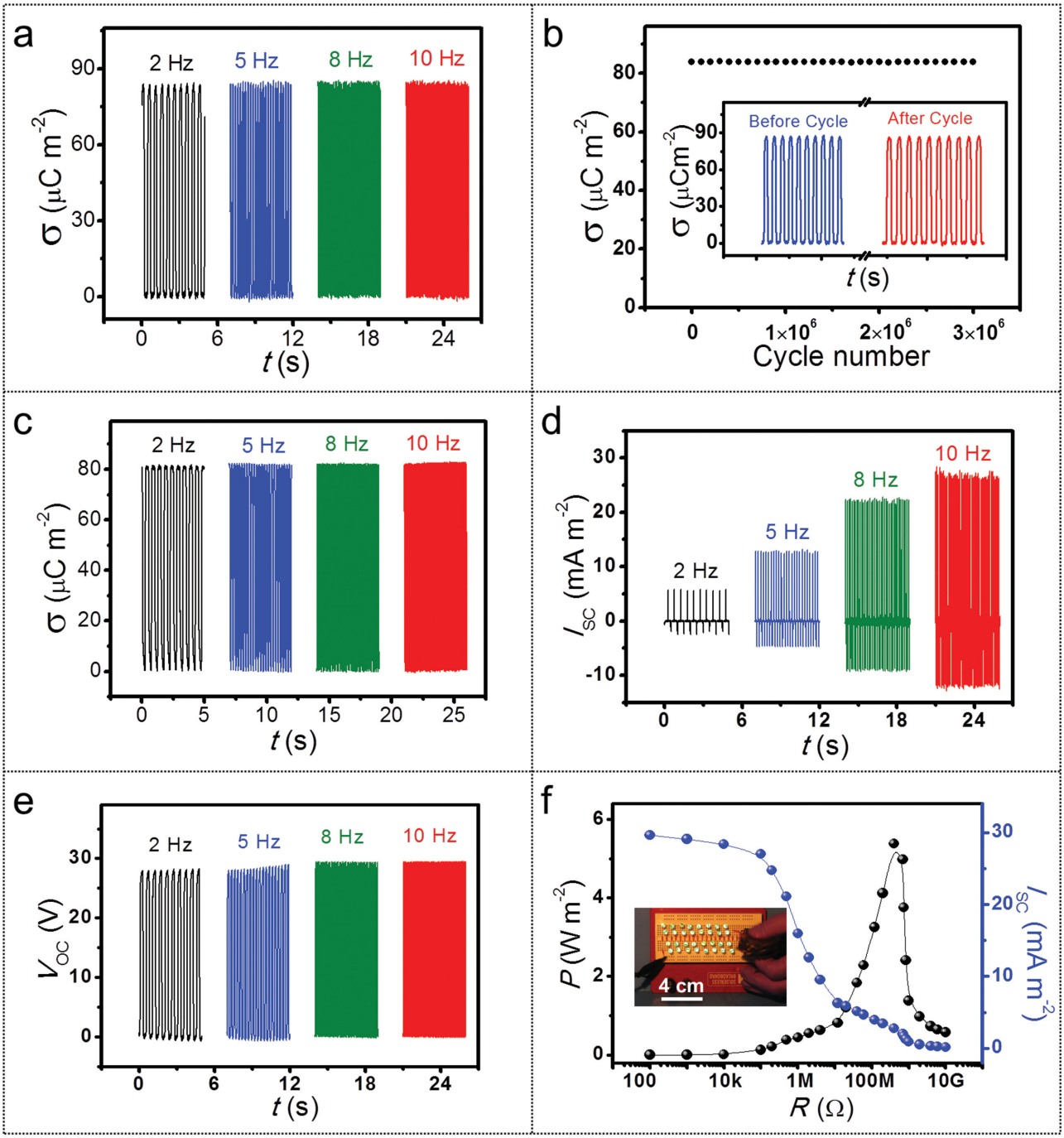

Figure 2. Output performance of the all-plastic-materials based TENG. a) Triboelectric surface charge density at various frequencies and b) cycling stability of a single hPPy-based TENG, inset shows the charge density before and after three million cycles at 10 Hz. c) Triboelectric surface charge density, d) short-circuit current density, and e) open-circuit voltage of the 3-parallel hPPy-based TENG at various frequencies. f) Current density and power density of the 3-parallel TENG at various loads, inset shows 32 LEDs lit up by pressing them manually.

to the single supercapacitor can be found in Figure 3d,e. At a current load as low as 5 μA, the discharging capacitance (C) of the 4-series supercapacitors is close to its charging one, owing to a very low leak current of around 0.4 μA, and its discharging/charging efficiency (η) increases as the current load (i) grows (Figure 3f). At a load of 200 μA, the power density of the supercapacitor is up to 3.13 W g^{-1}. These ensure the hPPy-based supercapacitors as an efficient energy storage unit for TENG.

To demonstrate the TENG-SC self-charging power system, three TENG connected in parallel are used to charge four supercapacitors connected in series via a rectifier and a switch K1, and then a load is connected via the other switch K2

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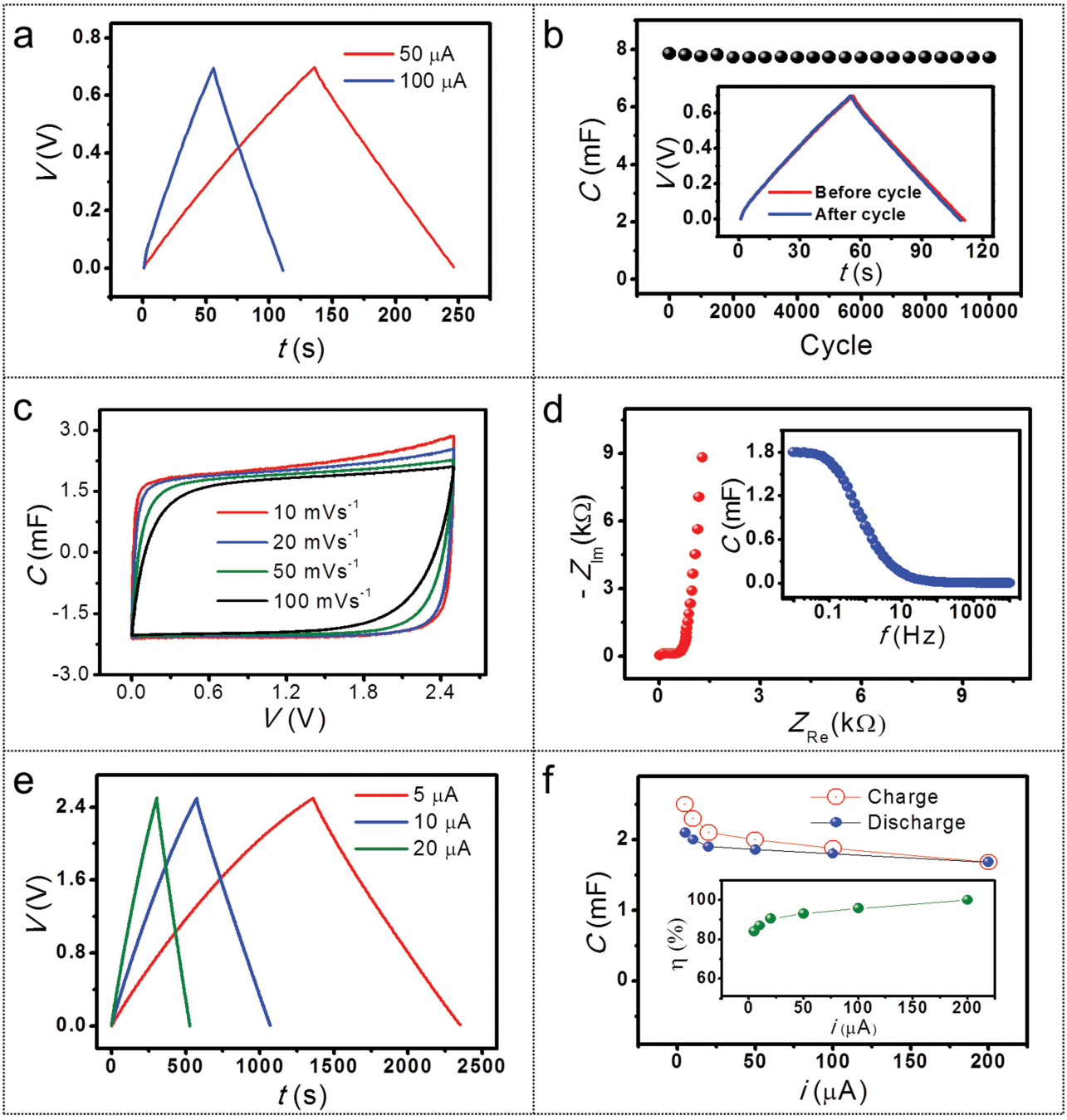

Figure 3. Capacitance properties of the all-plastic-materials based supercapacitors. a) GCD curves at different current density and b) stability of a single supercapacitor. c) CV curves at various scanning rates, d) Electrochemical impedance spectroscopy, with an inset plot of capacitance versus frequency, e) GCD curves at different current density, and f) charging/discharging specific capacitance as a function of current density of 4-series supercapacitors, inset shows the coulombic efficiency.

(**Figure 4**a). The package dimension of the power system is only 3 cm × 3 cm × 5 cm (Figure 4b). When K1 is on and K2 is off, the TENG that are triggered by a shaker begin to charge supercapacitors, the charging rate of which increases with the contacting frequency (Figure 4c). Taking 8 Hz as an example, it takes 4887 s (≈1.36 h) to charge from 0 to 1.5 V, and then takes 1449 s to discharge to 0 V at a current load of 2 μA (Figure 4d). When they are pressed simply by human fingers, the TENG can charge the supercapacitors from 10 to 40 mV in 30 s (Figure 4e), with the average charging current of 2.5 μA. When K1 is off and K2 is on, the supercapacitors can drive a calculator to perform a series of calculations continuously, like the four complex arithmetic shown in Video S3 (Supporting Information), which demonstrates that the self-charging power system can sustainably drive an electric device.

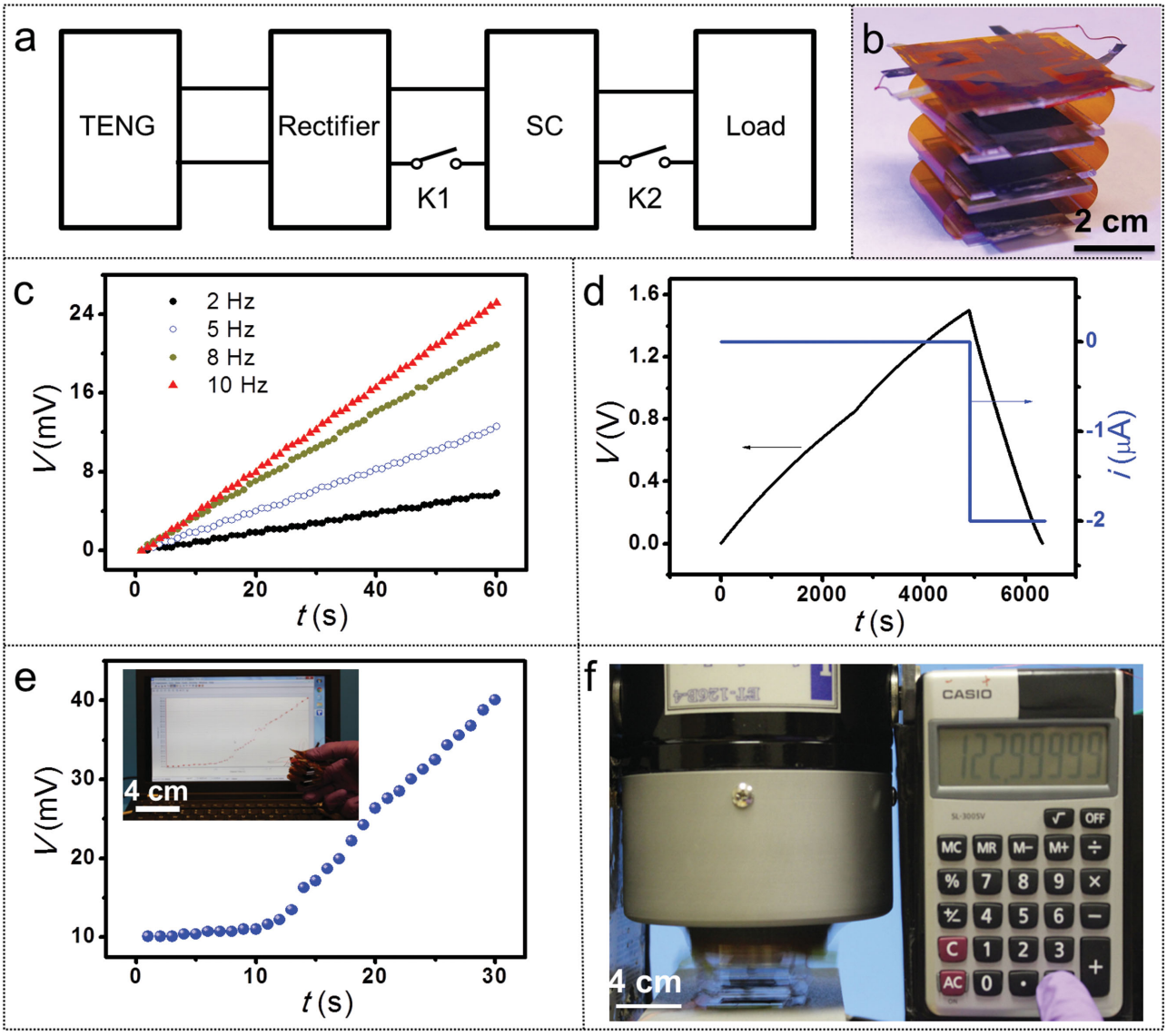

Figure 4. Performance of the all-plastic-materials based self-charging power system. a) Circuit diagram and b) image of the self-charging power system. c) Charging curves of the 4-series supercapacitors charged by the all-plastic 3-parallel TENG at various frequencies. d) Charging curve of the supercapacitors charged by the TENG at 8 Hz and discharged at the current load of 2 μA. e) Charging curve of the supercapacitors charged by pressing the TENG manually with the inset showing the image of the charging process, and f) a calculator is driven by the self-charging power system.

3. Conclusions

In summary, we have replaced the conventional metal electrode material for TENG by PPy and integrate it with PPy-based supercapacitors to build an all-plastic-materials based self-charging power system for the first time. The output power density of all-plastic TENG is further boosted by a tunable micro/nanostructure modification that effectively enlarges the contacting area and contact intimacy between triboelectric layer and dielectric layer. The fast charging ability and excellent stability of the all-plastic supercapacitors enable it as an efficient energy storage unit for TENG. Simply pressed by human fingers, the integrated all-plastic self-charging power system is able to drive an electronic device sustainably. With these excellent performances, the new power system can be a practical solution for many applications, from popular wearable electronics to large-scale blue energy harvesting in vast ocean.

4. Experimental Section

Synthesis of hPPy Electrodes: Pyrrole monomer (Py, Capchem, 99%) was twice distilled prior to use. The p-toluenesulfonic acid (TOSH, China Medicine Group, AR) and sodium p-toluenesulfonic (TOSNa, China Medicine Group, CP) were used as received. The polymerization solution contained 300 × 10^{-3} M pyrrole, 100 × 10^{-3} M TOSH, and 400 × 10^{-3} M TOSNa. The electrodeposition was carried out in a three-electrode cell with titanium sheet as working electrode and counter electrode, and a saturated calomel electrode (SCE) as refer electrode.

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The hPPy films were deposited on titanium electrodes by a pulse potentiostatic method, where the pulse parameter is a high potential of 0.75 V versus SCE, a high potential period of 0.04 s, a low potential of –0.2 V versus SCE and a low potential period of 0.12 s. The cPPy films were synthesized by galvanostatical method with a current density of 2 mA cm^{-2}.

Fabrication of the All-Plastic TENG: Two pieces of cast acrylic glasses were used as substrates (3 cm × 3 cm × 0.6 cm), and Kapton films with a thickness of 125 μm as spacers. PTFE film with a thickness of 25 μm as dielectric layer was adhered on PPy film as back electrode and then was adhered on a substrate. Subsequently, a piece of hPPy (1.7 cm × 1.7 cm) was adhered onto the substrate at the corresponding position as triboelectric electrode. Finally, conducting wires were connected to the two PPy electrodes as lead wires for electrical measurements.

Fabrication of All-Plastic Supercapacitors: The H_3PO_4 /PVA gel electrolyte was prepared as follows: 5g H_3PO_4 was added into 50 mL deionized water, and then 5 g PVA powder. The mixture was heated to 85 °C under stirring until the solution became clear. The synthesized hPPy electrodes were immersed into PVA/H_3PO_4 solution for 10 min, with their two-end parts kept above the solution. After being taken out, every two electrodes were assembled face to face onto a Kapton film substrate, leaving aside the bare part as the electrode terminal. Then, they were fully covered by a piece of Kapton film on top, the all-plastic SC was obtained.

Characterization: A Hitachi SU8010 field emission scanning electron microscope (SEM) was used to measure the morphology of the PPy electrodes. The static contact angle of water on hPPy was measured using contact angle meter (Solon Tech) with a charge coupled device (CCD) camera. A potentiostat (Princiton Application Research) was utilized to test the capacitance properties by using EIS, CV, and GCD techniques and the leak current by using Chronoamperometry method. For the electric output measurement of the TENG, a shaker motor (Labworks SC121) was applied to drive the TENG contact and separate, a programmable electrometer (Keithley model 6514), and a low noise current preamplifier (Stanford Research System modelSR570) were adopted to test the open-circuit voltage and short-circuit current, respectively.

Supporting Information

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

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