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Self-Powered Electrochemical Synthesis of Polypyrrole from the Pulsed Output of a Triboelectric Nanogenerator as a Sustainable Energy System

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Triboelectric nanogenerators (TENG) are able to convert mechanical energy into electricity. In this work, a self-powered electrochemical synthesis circle is designed, in which the electrode material of the TENG, polypyrrole (PPy), is prepared by the pulse output of the PPy-based TENG itself. The TENG based on PPy from self-powered synthesis (SPSPPy) presents a competitive performance compared to those made from commercial pulse sources. A supercapacitor that is fabricated from SPSPPy has a far superior performance than that synthesized by the conventional galvanostatic method. Furthermore, a self-charging power system that integrates a TENG and a supercapacitor is demonstrated to drive an electronic device sustainably. Moreover, the polymerization efficiency is optimized in TENG-based electrochemical synthesis because its high voltage can sustain multiple reactors simultaneously. Its upper limit is theoretically analyzed for optimal energy utility, and a maximum number of 39 reactors can be powered experimentally. Hence, TENG is validated as an effective pulse generator for the synthesis of PPy as well as other electrochemical technology, and this work greatly improves the understandings of TENG-based self-powered electrochemical systems.

1. Introduction

Renewable, environmental friendly, and sustainable power sources have been extensively explored during recent years. Meanwhile, the next-generation electronics, such as portable and wearable devices, bring forward more demand on flexible power providers with light weight, small size, and high-energy density.[1–3] These demands are exactly met by triboelectric nanogenerators (TENG), which have been demonstrated as an effective and low-cost energy harvester of various mechanical motions such as vibration, human walking, rain drops, air/water flow, etc.[4–16]

The TENG is based on the conjunction of triboelectrification and electrostatic induction. It generally consists of dielectric films such as polytetrafluoroethylene (PTFE) and electrodes which are conventionally metal, such as copper and aluminum, but recent reports show that polypyrrole (PPy) and graphene are excellent alternatives.[17,18] When the dielectric film is contacted by another material with distinct electron affinity, it acquires triboelectric charges that are immobile and difficult to be conducted away. Once they are separated, induced charges with opposite signs can be found in electrodes attached to them, and the potential drop drives electrons to flow, where a pulse current is formed. If they approach each other again by external force, the induced charges are gradually reduced and the electrons flow back. Thus, periodical contact and separation in TENG produces pulsed alternating current in micro- or milliampere scale.[19]

Generally, the pulse output of TENG needs to be transformed into constant current to drive most electronic devices that require a stable and continuous input power.[20,21] However, there are some potential applications preferring pulsed input, involving pulsed charger for batteries and pulsed electrodeposition method for many materials.[22,23] A good example is to electrochemically polymerize PPy by pulsed current to serve as electrode material for TENG and electrochemical supercapacitors.[17] PPy is stable, low cost, high conducting, and environmental friendly, difficult to be oxidized or corroded even in harsh environments. Compared with PPy prepared via constant current, pulse-synthesized PPy is reported to exhibit higher electronic conductivity with micro/nanostructured surface,[24,25] which provides higher contact intimacy than metal does. As previously reported, TENGs that are fabricated by using pulse-synthesized PPy can significantly outperform metal-based ones in charge density, a key performance parameter of TENG. And the supercapacitors based on pulse-synthesized PPy obtain better performance

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as well.[17] Meanwhile, TENG is a natural pulse generator with parameters involving frequency and magnitude easily configured by the input mechanical motion, i.e., the triggering frequency and displacement, correspondingly. It has been reported that some self-powered electrochemical systems based on TENG have applied in applications involving seawater desalination, water splitting, and cleaning of air pollution.[26–30]

Based on this, an interesting self-powered synthesis circle of PPy can be established that PPy, the electrode material of TENG, is synthesized by the pulse output of TENG. Attribute to the high-output voltage of TENG, the reactors can be connected in series, which will greatly enhance the average power. In this work, we verified this self-powered synthesis circle and demonstrated TENG as an effective pulse generator in electrodeposition technology TENGs and supercapacitors are fabricated by using the PPy from self-powered synthesis (SPSPPy), and they are further integrated into a self-charging power system (SCPS). A digital temperature–humidity meter is powered by the self-charging power system as a demonstration. Since it is also an all-plastic-materials-based system, well durability and environmental benignancy can be guaranteed. This work validates TENG as an effective pulsed power source for electrodeposition process, and greatly improves our understandings on TENG-based self-powered electrochemical system.

2. Results and Discussion

The self-powered synthesis cycle of PPy is illustrated in **Figure 1**a. With horn-like morphology of PPy (hPPy) prepared by a commercial pulse source (Potentiostat, Princeton Application Research) as electrodes in size of 4 cm × 4 cm, the all-plastic-materials-based TENG is reported to achieve as twice charge density as that of metal-based one.[17] This TENG is used as an initial pulse source of the self-powered synthesis cycle. Three of the all-plastic TENGs are stacked together and connected in parallel to improve their current output. The TENGs are connected with several reactors in series through a full-wave rectifier to prepare PPy. Their total short-circuit charge transfer $Q_{SC,max}$ is 0.36 μC and short-circuit current $I_{SC,max}$ is 68 μA at a frequency of 10 Hz (Figure S1a,b, Supporting Information), and hence its charge density is calculated as 75 μC m^{-2}. More TENGs can be employed if the self-powered synthesis process needs to be accelerated, as the parallel connection of TENG will increase output current. If enlarging displacement in each TENG, which will increase the output voltage, more reactors can be supported at the same time. Here in our experiment, we tried reactor number (N) from 1 to 9. The horn-like morphology of PPy prepared from the self-powered synthesis cycle is displayed in Figure 1b. The micro/nanostructure horns grow on its surface to form dense

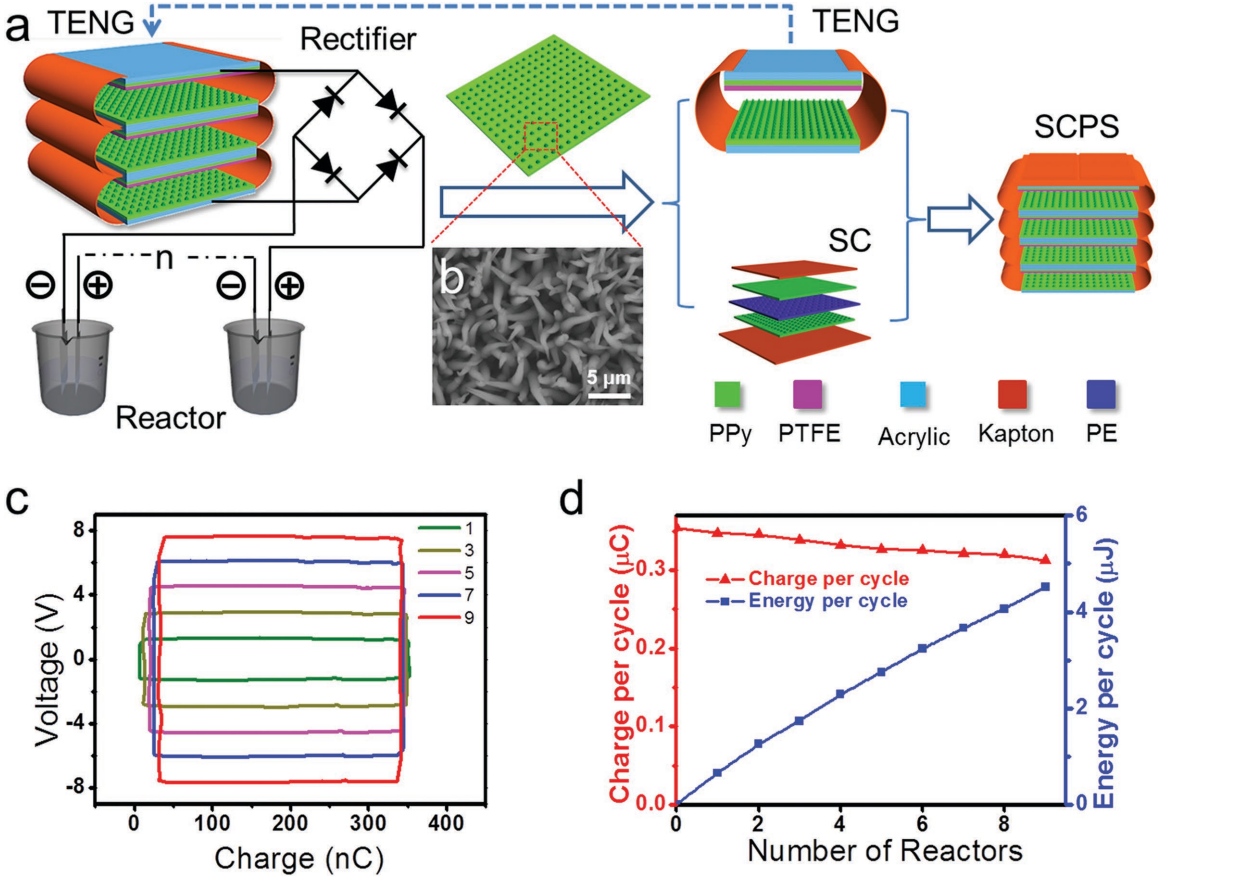

Figure 1. Overview of the self-powered synthesis system. a) Schedule of the self-powered synthesis system, b) SEM image of hPPy synthesized by the system, c) voltage–charge plot of the self-powered synthesis system at various reactors, and d) charge per cycle and energy per cycle of the system as function of number of reactors.

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and homogeneous arrays, with a length of 4–6 μm and approximate micro/nanohorns density as 10^6–10^7 cm^{-2}. The unique micro/nanostructure on the surface of hPPy can enlarge the effective contact area and improve the contact intimacy and hence enhance the contact electrification for TENGs.[17] Based on the SPSPPy, an all-plastic TENG and an all-plastic supercapacitor are fabricated. The hPPy-based TENG can not only be integrated as an SCPS with the hPPy-based supercapacitor but also used as a new pulse source to synthesize the hPPy to form a self-powered synthesis cycle.

To optimize the polymerization efficiency (defined as total utilized energy per cycle E_U over the largest energy output per cycle E_m of TENG) during the synthesis process, the voltage–charge (V–Q) plot is adopted as the analytical tool to reveal the relation between the E_U and N.[31] The details of measurement are described in the Supporting Information. When N is increased, the total voltage required for synthesis reaction V_C is rapidly increased, while the transferred charge per cycle Q_C is slightly declined, which of nine reactors only decreased 13.4% compared to that of one reactor (Figure 1c). This phenomenon in synthesis is similar to that of utilizing TENG to charge batteries as reported.[32] Although this mild declining of Q_C leads to prolong slightly synthesis time in case of nine reactors, the polymerization efficiency is 7.8 times as that of one reactor.

All these V–Q plots are also inscribed with the plotted cycle of maximized energy output with infinite load resistance as shown in the dashed line in Figure S1c (Supporting Information). Since both $V_{OC,max}$ (the maximum open-circuit voltage) and V'_{max} (the maximum voltage at $x = x_{max}$) are far higher than the voltage for reactions V_C (Supporting Information), due to the reported Equation (1) in ref. [32], the following equation can be easily derived

$$Q_c = \frac{E_c}{V_c} = 2Q_{SC,max}(1 - V_c/V_{OC,max} - V_c/V'_{max}) \approx 2Q_{SC,max} \quad (1)$$

Here, E_C presents the total energy consumed per cycle in reactions, including E_U and the energy loss in the rectifier (see Equation (S1), Supporting Information). Therefore, all the Q_C tested should be nearly two times of $Q_{SC,max}$, which is consistent with experimental results as shown in Figure 1c. Note that V_C includes the voltage drop across the diodes in the rectifier V_R, which is about 0.62 V. Consequently, E_U increases almost linearly with N when N is small (Figure 1d). If N further increases, E_U also increases until

$$V_C = V_R + \frac{1}{2}\frac{V_{OC,max}V'_{max}}{V_{OC,max} + V'_{max}} \quad (2)$$

which is about 31.65 V, where the optimized reactor number can be derived as 39 or 40. Meanwhile, the maximum polymerization efficiency is calculated to be about 21% (see the

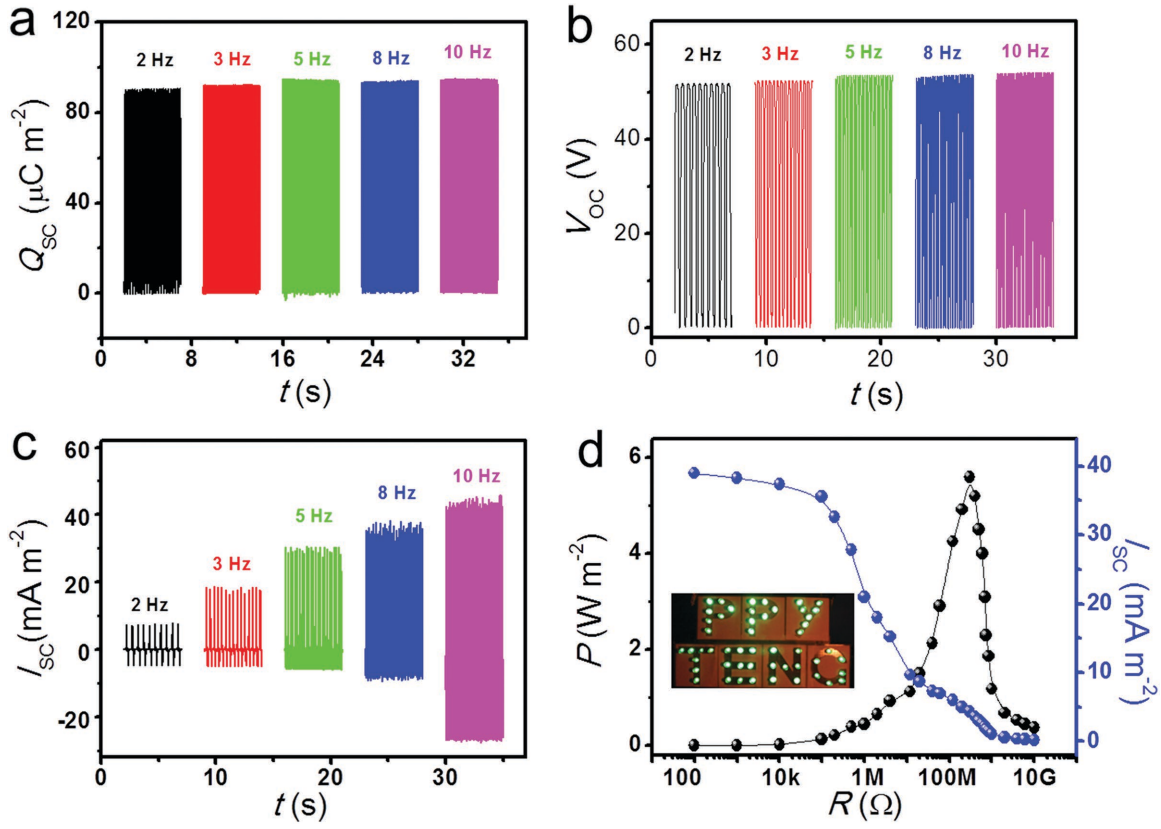

Figure 2. Output performance of the TENG based on PPy from self-powered synthesis. a) Triboelectric surface charge density, b) open-circuit voltage, and c) short-circuit current at various frequencies; d) Current density and power density of the TENGs at various loads, inset shows LEDs lit up by pressing them manually, saying "PPy TENG."

Supporting Information for the measurement details and calculation methods).

Based on SPSPPy, an all-plastic TENG and an all-plastic supercapacitor are fabricated. In TENGs, PTFE is used as a triboelectric layer and hPPy as the other triboelectric layer and electrode, as called the triboelectric electrode. The performance of a single TENG fabricated with the SPSPPy was test with frequency range from 2 to 10 Hz. Its triboelectric surface charge density (σ) and open-circuit voltage ($V_{OC,max}$) are about 90 μC m^{-2} and 52 V, respectively, and they are nearly stable with various frequencies (**Figure 2**a,b). The charge density is slightly greater than that of PPy-based TENG using the commercial pulse generator to prepare its electrode material. Its short-circuit current ($I_{SC,max}$) increases with frequencies, from 8 mA m^{-2} at 2 Hz to 45 mA m^{-2} at 10 Hz (Figure 2c). Its power density reaches maximum, about 5.8 Wm^{-2}, when the resistance is around 400 M Ω. Simply pressed by human finger, this TENG can light up dozens of LEDs, demonstrated in the inset of Figure 2d and Video S1 (Supporting Information). This validates TENG itself as an effective pulse generator in electrochemical deposition process.

In supercapacitor (SC), hPPy is applied as the electrode active material of both anode and cathode, while porous polyethylene film and H_3PO_4/PVA (polyvinyl alcohol) gel are adopted as separator and electrolyte. To further confirm that TENG-based electrodeposition is also suitable for supercapacitors, performance of PPy-based supercapacitors was further compared, where the PPy electrodes were synthesized by pulsed output from TENG (noted as SPSPPy-SC) and by galvanostatic method (named as GPPy-SC), a conventional constant current technique (Figure S2, Supporting Information), respectively. In the electrochemical impedance spectroscopy (EIS) curve (**Figure 3**a), the imaginary part of impedance of SPSPPy-SC is more vertical to the real part than that of G-PPy SC, indicating the former with better capacitive behavior.[33] Besides, a much wider high-capacitance plateau is found in the SPSPPy-SC (the inset in Figure 3a), which signifies its faster charging/discharging ability. Two rectangle-like cyclic voltammetry (CV) curves at a scanning rate of 10 mV s^{-1} suggest they both having fast electrochemical switch ability,[34] but the SPSPPy-SC evidently has greater capacitance in the entire potential window (Figure 3b). Although the voltage of GPPy-SC is linear in the entire window with no obvious ohm-drop phenomenon in galvanostatic charging/discharging (GCD) analysis at a low-current load of 5 μA (Figure S3a, Supporting Information), it presents slight but notable ohm-drop phenomenon (Figure 3c) at 40 μA. The voltage of SPSPPy-SC is linear without any obvious ohm-drop even at a current load of 80 μA (Figure S3b,

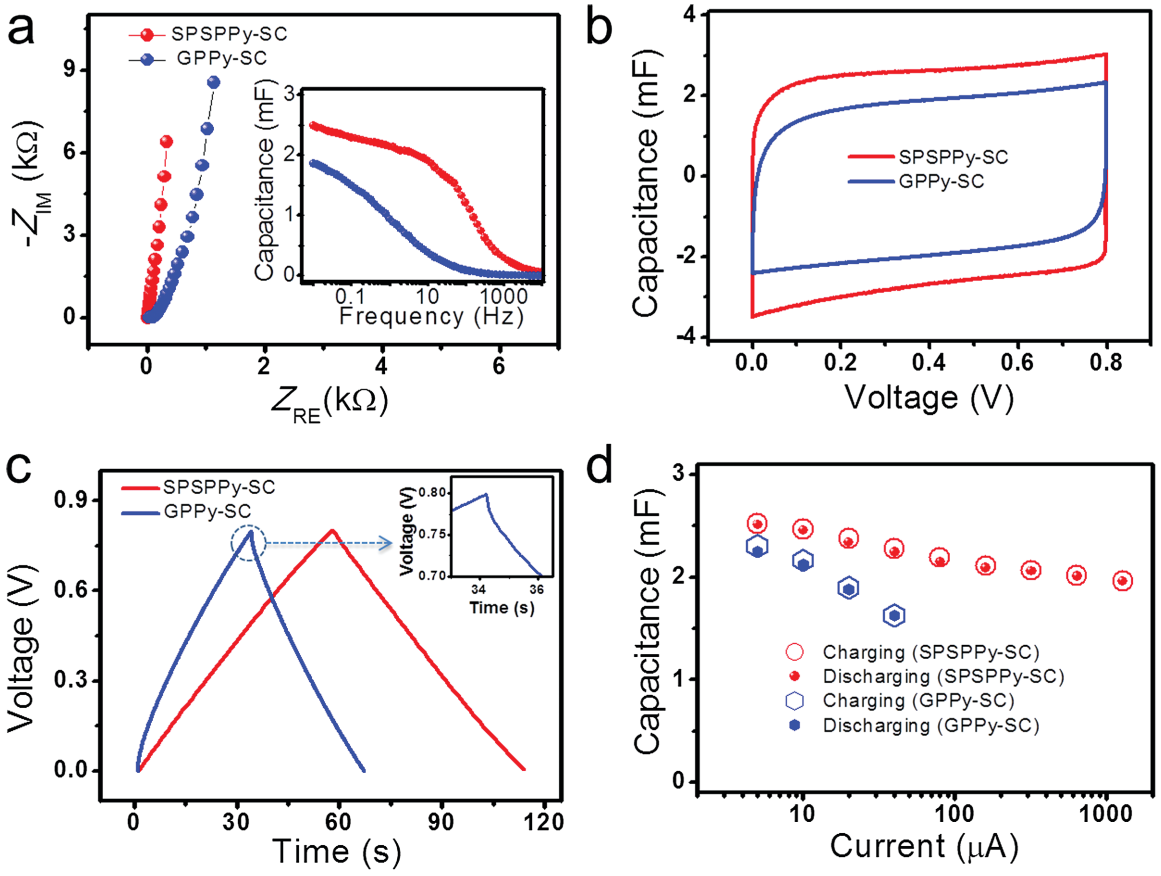

Figure 3. Capacitance properties of the supercapacitor based on PPy from self-powered synthesis (SPSPPy-SC) and galvanostatic synthesis (GPPy-SC). a) Electrochemical impedance spectroscopy, with an inset plot of capacitance versus frequency, b) CV curves at a scanning rate of 10 mV s^{-1}, c) GCD curves at a current load of 40 μA, and d) charging/discharging specific capacitance as a function of current density.

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Supporting Information), which reveals a very small inner resistance and very fast charging–discharging ability of self-synthesized supercapacitor. Their discharging capacitances are calculated as 2.45 mF for SPSPPy-SC and 2.2 mF for GPPy-SC. As the current load increases, the discharging capacitance of SPSPPy-SC is almost identical to charging capacitance, which is attributed to its very low-leakage current of around 100 nA (Figure 3d). Meanwhile, its capacitance remains very stable with the increasing of current load. However, the capacitance of GPPy-SC decays fast with the increasing current load. The excellent capacitance properties of the self-synthesized PPy can be explained by two reasons: one is that the micro/nano-structure of the PPy can greatly improve the specific surface area; the other is that a high-electronic conductivity and better molecular anisotropy can be achieved by the pulse synthesis method.[29,30] In a word, TENG is validated as an effective pulse generator for electrodeposition process again.

In order to drive electronic devices that require a stable and continuous input power, a self-synthesized self-charging power system is integrated with four TENGs in parallel and four supercapacitors in series by a full-wave rectifier (**Figure 4**a), where their electrode materials, the hPPy, are all produced by pulsed output from TENG. In the self-charging power system, several TENGs (typically four) are stacked together and connected in parallel to improve the output charge and current and four supercapacitors are connected in series to improve the output voltage of the power system. When K1 is switched on and K2 is switched off, the supercapacitor is charged by TENGs. Although the size of the self-charging power system is only 3 cm × 3 cm × 4 cm (Figure 4b), its voltage increases from 0 to 18.5 mV during 100 s at a mechanical triggering frequency of 5 Hz, and its voltage grows faster with the increasing triggering frequency, from 0 to 0.31 V at a frequency of 10 Hz during 100 s (Figure 4c) and to 1.5 V during 678 s (Figure 4d). When K1 is switched off and K2 is switched on, the supercapacitor discharges to 0 V in 376 s at the current of 4 μA, indicating an equivalent galvanostatic current of 2.2 μA at a frequency of 10 Hz. Besides, it is 1.31 and 1.89 μA at frequencies of 5 and 8 Hz, respectively. When both K1 and K2 are on, the self-charging power system can sustainably drive a digital temperature–humidity measure (the inset in Figure 4d and Video S2, Supporting Information).

3. Conclusions

In summary, we report a self-powered electrochemical synthesis of PPy as driven by a TENG-based self-powered system,

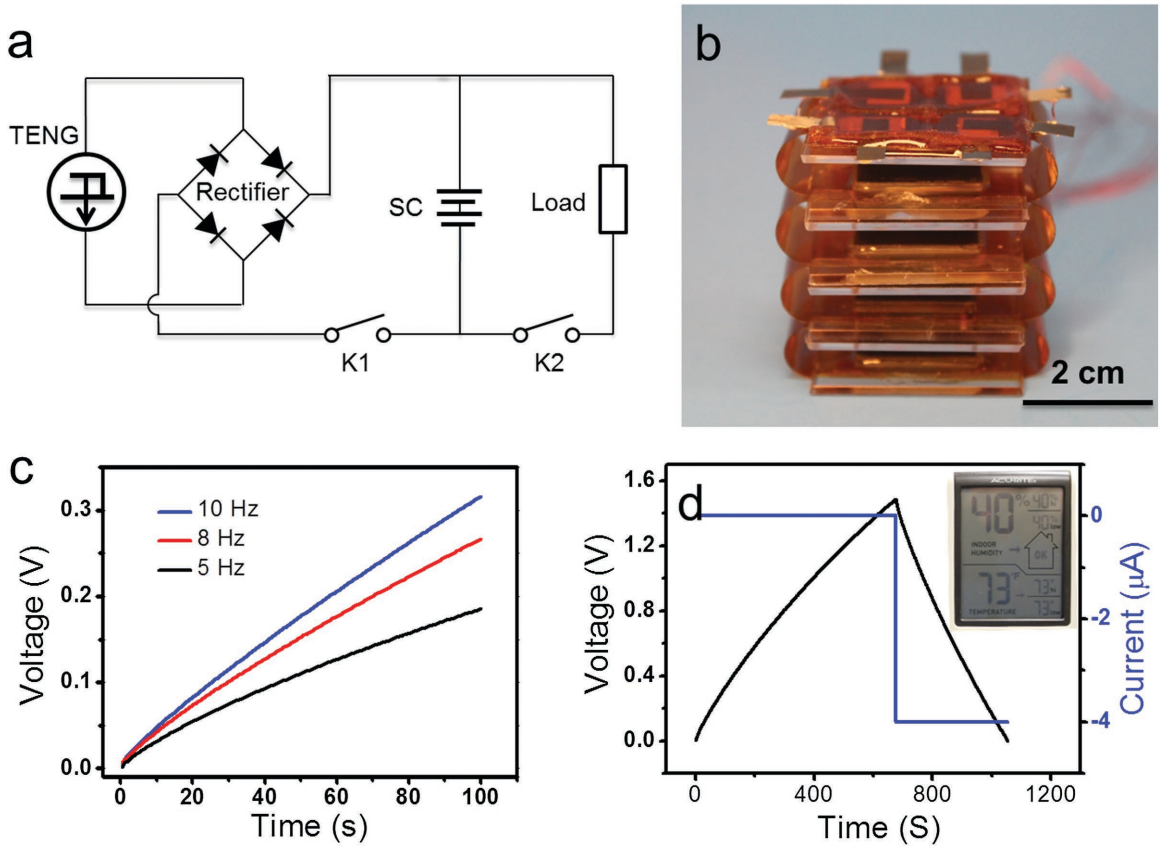

Figure 4. Performance of the self-charging power system based on PPy from self-powered synthesis. a) Circuit diagram and b) image of the self-charging power system; c) charging curves of the supercapacitors charged by the TENGs at various frequencies, d) charging curve of the supercapacitors charged by the TENGs at 10 Hz and discharged at the current load of 4 μA, the inset shows that digital temperature–humidity is driven by the self-charging power system.

and the outstanding performances of the self-synthesized PPy as electrode material for TENG and SC to form a self-charging powering system. For PPy-based TENG, the performance of PPy prepared via pulsed output from TENG is competitive to those prepared by a commercial pulse generator. While for PPy-based supercapacitors, the capacitance properties of pulse-synthesized PPy are far superior to that synthesized by a constant current method. Furthermore, the self-charging power system integrated from TENGs and supercapacitor that all adopt self-synthesized PPy electrodes is demonstrated to be able to drive electronic device sustainably. Our work validates TENG as a natural and effective pulse generator that can be applied in electrochemical technology for materials synthesis.

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 two-electrode cell with titanium sheet as working electrode and counter electrode. The synthesized PPy films were deposited on titanium electrodes by a rectified pulse-output of PPy-based TENG at a frequency of 10 Hz, where the PPy in TENG were deposited on titanium electrodes by a pulse potentiostatic method, with the pulse parameters of 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.

Fabrication of the All-Plastic TENGs: Two pieces of cast acrylic glasses were used as substrates (3 cm × 3 cm × 0.3 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 one of the self-synthesized PPy films as back electrode and then was adhered on a substrate. Subsequently, another piece of PPy (2 cm × 2 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 PVA/H_3PO_4 gel electrolyte was prepared as follows: 5 g 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 self-synthesized PPy 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. When the PVA/H_3PO_4 gel solidified at room temperature, 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 (Princeton 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 output-performance measurement of the TENG, a shaker motor (Labworks SC121) was applied to drive the TENG to 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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