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Flexible Self-Charging Power Cell for One-Step Energy Conversion and Storage

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Energy conversion and storage,[1–3] as the two most important technologies for energy, are usually two distinct processes that are performed by using two different and separated physical units, such as a piezoelectric nanogenerator and lithium-ion battery.[4–9] Recently, we presented a novel fundamental mechanism that directly hybridizes the two processes into one, through which mechanical energy is directly converted into and simultaneously stored as electrochemical energy.[10] When the traditional separator film of a lithium-ion battery is replaced with a piezoelectric film, the internal piezoelectric potential created by mechanical strain can drive lithium ions to migrate toward the anode. Based on this new piezoelectric-potential-driven electrochemical (piezo-electrochemical) approach, a self-charging power cell (SCPC) has been fabricated for directly converting mechanical energy into electrochemical energy.[10] The first prototype of the SCPC with TiO_2-nanostructured anodes was sealed in a rigid stainless-steel 2016-coin-type cell, which is hard and absorbs a large proportion of the mechanical energy generated; this results in a rather low conversion efficiency.

Herein, we report the first flexible SCPC. By using a kapton film as a supporting shell, flexible graphene materials and piezoelectric polyvinylidene fluoride (PVDF) separator are sealed in liquid electrolyte. The flexible SCPC can be efficiently charged by means of a tiny mechanical agitation, such as finger pressing or the compaction due to rolling of a bicycle tire. Development of flexible SCPCs is an important step for practical applications of SCPCs in our living environment.

The experimental design of flexible SCPCs involves replacing rigid device structures and electrodes with flexible materials, as schematically shown in **Figure 1**a,b. A flexible SCPC is composed of four major components: electrodes, well-polarized

PVDF separator, liquid electrolyte, and flexible shell. Similar to the prototype of SCPC, a layer of flexible polarized PVDF film is located between the anode and cathode as the separator. This PVDF film can establish a piezoelectric potential across its thickness under externally applied stress,[11–13] which not only converts mechanical energy into electricity but also serves as the driving force for the migration of Li ions. The shells are kapton boards, which are much more flexible than the traditional rigid stainless-steel shell. In Figure 1b it can be seen that the flexible SCPC can be bent by more than 90°. Such a flexible structure would make it more convenient for the conversion and storage of small amounts of mechanical energy in the living environment as electrochemical energy than would a rigid stainless-steel shell structure. Figure 1c is a typical SEM image of the graphene nanosheets used as anodes. Figure 1d shows the PVDF film; the thickness of the film with porous structures is about 100 μm. Periodic compressive stress, such as that arising from a finger pressing, can be applied to the flexible SCPC to charge it, as shown in Figure 1e.

The piezoelectric output properties of the PVDF film were measured after sealing PVDF in Kapton shells without injecting
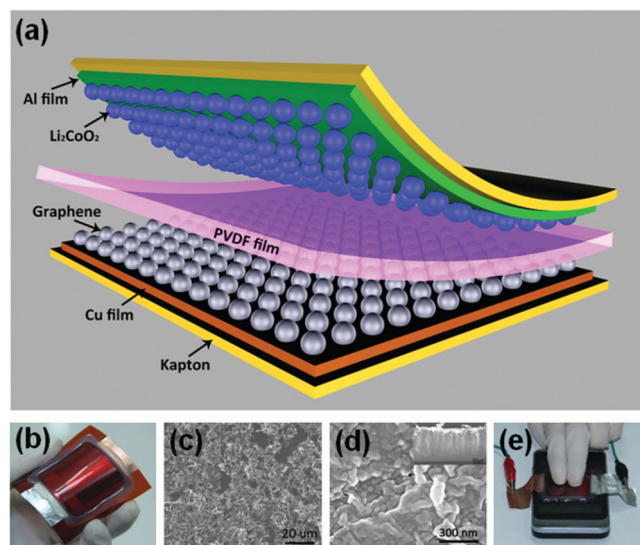
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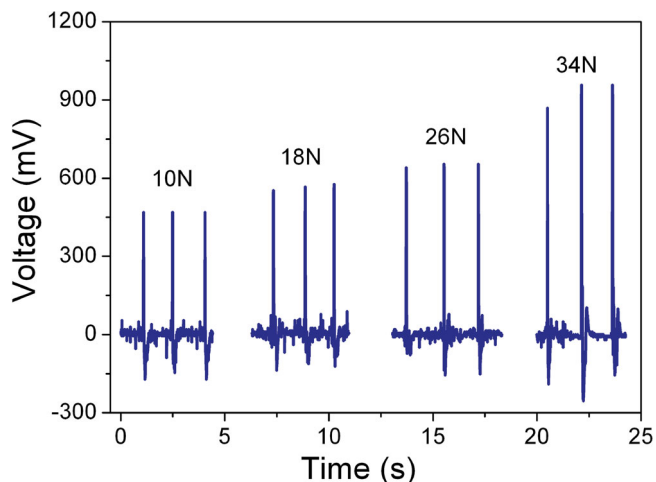Georgia Institute of Technology
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Figure 1. a) Schematic diagram showing the design of a flexible SCPC. Graphene nanosheet composites on copper foil are used as anode; a layer of polarized PVDF film performs as separator; the cathode is a $LiCoO_2$–based mixture on aluminum foil; Kapton boards are used as the shells of flexible SCPCs. b) Optical image of a flexible SCPC. c) Scanning electron microscope (SEM) image of flexible graphene nanosheets. d) Top-view SEM image of PVDF film. The inset shows the side-view SEM image. e) Periodic compressive stress from finger pressing is applied to a flexible SCPC to charge it.

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Figure 2. The piezoelectric output properties of the PVDF film under different applied forces.

Figure 3. a) Galvanostatic cycling charge/discharge profiles of a flexible SCPC before and after bending to ca. 60° using a DC power source to test the tolerance to mechanical deformation. Both measurements were performed at 2 C rate. b) Cycling performance at 4C rate of a flexible SCPC using DC power to charge it.

electrolyte under different applied forces, and Pt layers that act as electrodes are sputtered on both sides of the PVDF film. As shown in **Figure 2**, when the applied force is 10, 18, 26, and 34 N, the piezoelectric output voltage of the PVDF film is 469, 566, 654, and 957 mV, respectively. The strain of the PVDF film increases with increasing applied force, which results in higher piezoelectric output.

Recently, graphene has been confirmed as an excellent electrode material for lithium-ion batteries.[14,15] Here, graphene nanosheets are synthesized via a hydrothermal route and used as the anodes of flexible SCPCs.[16,17] To verify the reliability of the flexible SCPC, the electrochemical performance of a flexible SCPC is evaluated by galvanostatic charge/discharge tests. **Figure 3**a shows charge/discharge profiles of a flexible SCPC before and after bending to about 60° using a direct current (DC) power source to test tolerance to mechanical deformation. After bending the flexible SCPC, its capacity remains the same, which demonstrates that the electrochemical performance of the flexible SCPC does not change with bending. The cycling performance of the flexible SCPC is shown in Figure 3b. Through 30 cycles, the cyclability of the flexible SCPC is good and no leakage of electrolyte is observed.

Figure 4a shows a typical self-charging process under periodic compressive stress and the corresponding constant-current discharge process of the flexible SCPC. With a compressive force of 34 N applied to the flexible SCPC at a frequency of 1 Hz, the voltage of the device increases from 500 to 832 mV in 500 s. After the self-charging process, the device is discharged back to its original voltage of 500 mV over 957 s under a constant discharge current of 1 μA. In this case, the stored capacity of the flexible SCPC is about 0.266 μAh. The self-charging process is affected by the magnitude of the piezopotential that is related to the magnitude of the compressive force, as shown in Figure 4b. The first four cycles of Figure 4b are the self-charge and discharge cycle when only the mechanical force applied to the device was increased. When the applied forces were 18, 22, 26, and 30 N with a frequency of 1 Hz, the flexible SCPC was charged to 732, 769, 791, and 805 mV within 480 s, respectively.
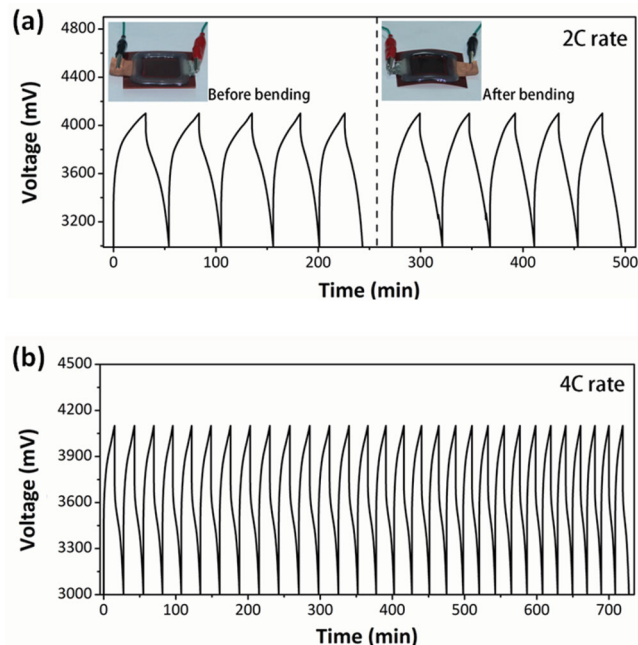
The self-charging effect is enhanced with increasing applied force. When both the force and the frequency are kept unchanged, as shown in the subsequent cycles of Figure 4b, the flexible SCPC is charged to similar levels. A series connection of several flexible SCPCs can drive a LED, as shown in the inset of Figure 4b. The Young's modulus of PVDF is ca. 2 GPa, thus a small force can generate enough strain for piezoelectric output of PVDF. It should be noted, however, that the relatively rigid Kapton shells absorb the mechanical energy, which results in a minimum force necessary to activate the self-charging process. When the applied force is 10 N, the piezoelectric output voltage of the PVDF sealed in Kapton boards is less than 500 mV (Figure 2) and the self-charging process is hardly activated. The stability of a flexible SCPC is good when charged via periodic deformation, as shown in Figure 4c. Through 30 cycles, as the force and the frequency are both constant, while the rate at which the voltage is increased and the discharge capacity are relatively stable. If the piezoelectric polarization of PVDF film is reversed, the piezoelectric field in the PVDF film points from anode to cathode, which will drive the migration of Li ions in the opposite direction. As a result, the reverse electrochemical process will take place by a similar mechanism, so that the entire device will be discharged under application of periodic compressive force. The response of the flexible SCPC fabricated using PVDF film with opposite polarization is measured under periodic compressive stress, as shown in Figure 4d. The voltage decreased from 577 to 405 mV in 660 s. The flexible SCPC can not only be charged by compressive strain energy, but can also absorb the strain energy of the bending deformation, as schematically shown in Figure 4e. With a bending

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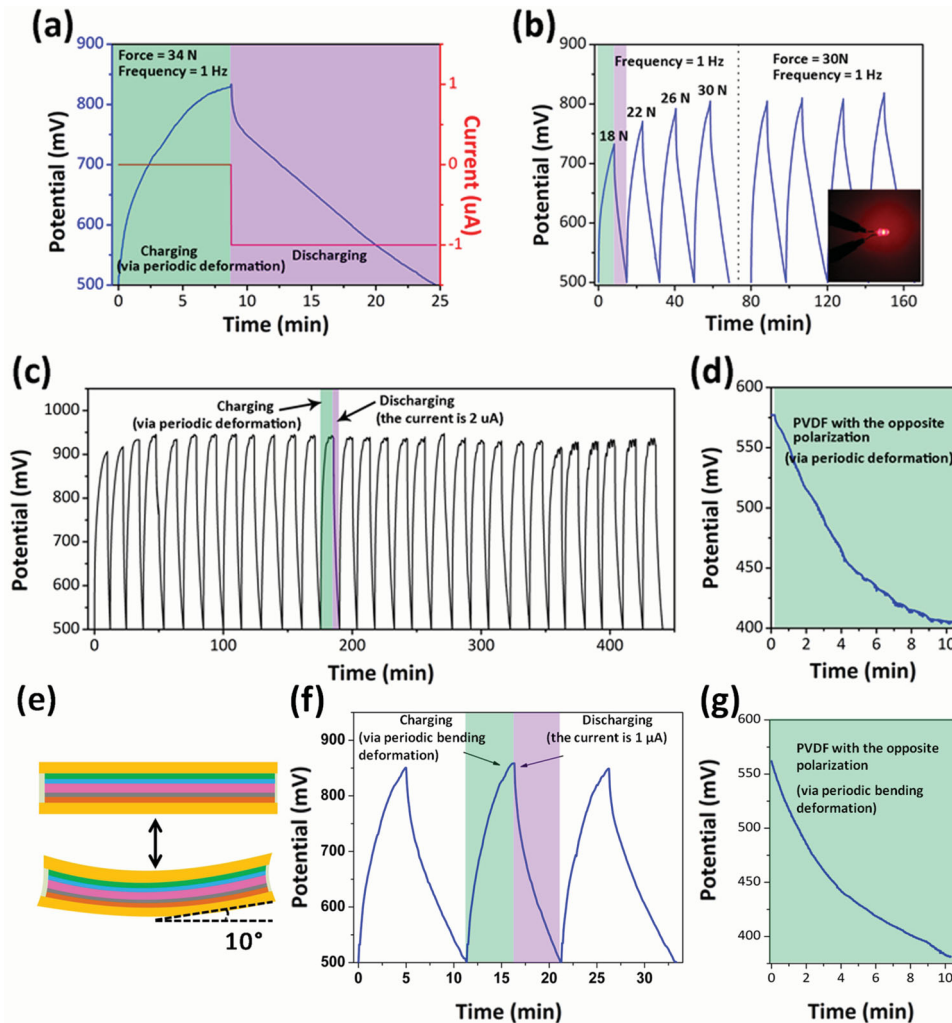www.advenergymat.de

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Figure 4. a) A typical self-charging process under periodic compressive stress and the corresponding discharge process of a flexible SCPC. The green shaded region denotes the self-charging process that occurs simply by applying periodic mechanical compressive strain to the device. The constant-current discharge process is denoted by the purple region, and the discharge current is 1 μA. b) Self-charging and discharging cycles of the flexible SCPC under application of different forces. The inset shows the operation of a LED using flexible SCPCs as the power source. c) Stability of a flexible SCPC charged via periodic deformation. The discharge current is 2 μA. d) For a flexible SCPC with the same structure but with the PVDF film having a reversed polarization that drives the Li ions in the opposite direction, there is no charging effect, which confirms the model proposed for SCPCs. e) Schematic image showing the self-charging process under periodic bending deformation. f) The self-charging and discharging cycles of the flexible SCPC under periodic bending deformation. g) Self-discharging behavior of a flexible SCPC that has the same structure but with the PVDF film having a reversed polarization under periodic bending deformation.

deformation (10°) applied at a frequency of 1 Hz, the voltage of the flexible SCPC increased from 500 to 850 mV in 300 s, as shown in Figure 4f. The response of the flexible SCPC fabricated using PVDF film with opposite polarization is measured under periodic bending deformation, as shown in Figure 4g. The voltage decreased from 562 to 381 mV in 660 s.

The working mechanism of the flexible SCPC is an electrochemical process driven by piezoelectric potential created by the deformation of PVDF. At the very beginning, the device is in a discharged state, with $LiCoO_2$ as the cathode and graphene as the anode, as shown in **Figure 5**a. The prepolarized PVDF film, which serves as the separator, has intimate contacts with both electrodes and would generate a positive piezoelectric potential (piezopotential) at the cathode ($LiCoO_2$) side

and negative piezopotential at the anode (graphene) when a compressive stress is applied to the device, as shown in Figure 5b. Under the piezoelectric field driven from the cathode to the anode, Li ions in the electrolyte migrate from cathode to anode through the PVDF film separator.[10,18] The piezopotential and the migration of Li ions drive the reaction at the cathode ($LiCoO_2 \leftrightarrow Li_{1-x}CoO_2 + {}_xLi^+ + {}_xe^-$) in the right direction, which resulting in deintercalation of Li ions from $LiCoO_2$ and the production of $Li_{1-x}CoO_2$,[19,20] as shown in Figure 5c. The reaction at the anode ($6C + {}_xLi^+ + {}_xe^- \leftrightarrow Li_xC_6$) move to the right direction, which results in intercalation of Li ions into graphene and the production of Li_xC_6.[14,21,22] During this process, Li ions continuously migrate from the cathode to the anode and the device is charged up a little. The piezoelectric
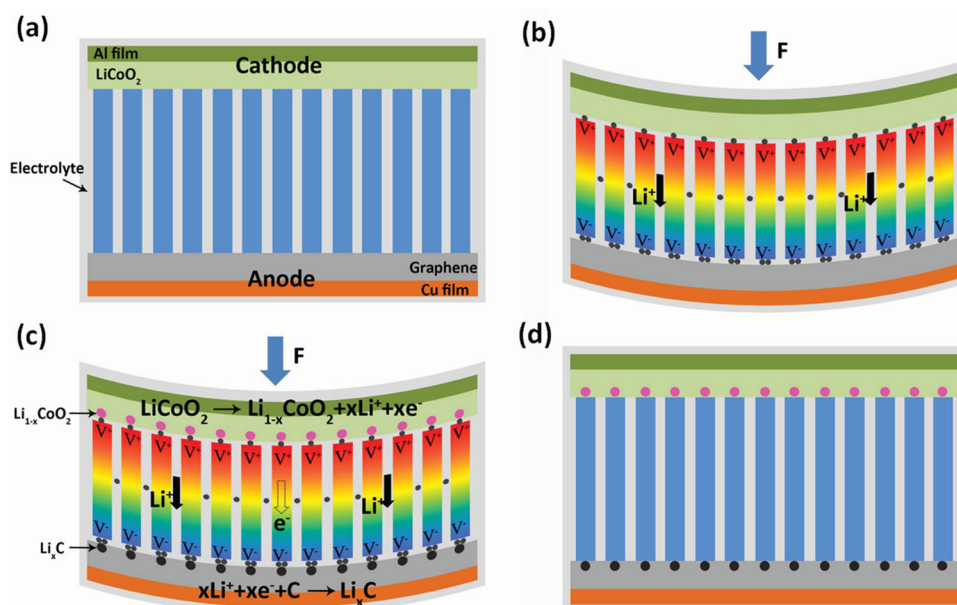
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Figure 5. The working mechanism of the flexible SCPC charged by compressive straining. a) Schematic illustration of the flexible SCPC in its discharged state with $LiCoO_2$ as cathode and graphene as anode. b) When a compressive stress is applied onto the device, the PVDF piezoelectric separator layer creates a piezoelectric field with the positive piezopotential at the cathode side and negative piezopotential at the anode. c) Under the piezoelectric field, Li ions will migrate through the PVDF film separator in the electrolyte from the cathode to the anode. d) After the applied force is released, the piezoelectric field of the PVDF disappears, and a cycle of self-charging is complete.

field drives the migration of Li ions until the distribution of the Li ions can balance the piezoelectric field in the PVDF film. When the applied force is released, the piezoelectric field of the PVDF disappears and a portion of Li ions diffuses back and an even distribution of Li ions is reached again (Figure 5d). This action completes one cycle of charging, which results in oxidization of a small amount of $LiCoO_2$ to $Li_{1-x}CoO_2$ and reduction of some graphene to form Li_xC_6. At the same time a small amount of mechanical energy is directly converted and stored as electrochemical energy. When the device is mechanically deformed again, the process presented above is repeated,

which results in another cycle of the charging process. In this self-charging mechanism, the role played by the piezoelectric material (PVDF) is similar to the DC power supply used in the conventional charging process of a Li-ion battery. The flexible structures can avoid the waste of mechanical energy through shells and electrodes, resulting in effective mechanical–electrochemical conversion and storage.

The flexible SCPC can conventionally convert and store small amounts of mechanical energy in our living environment, such as human-body and machine movement, as shown in **Figure 6**. The pressing action of human fingers can provide
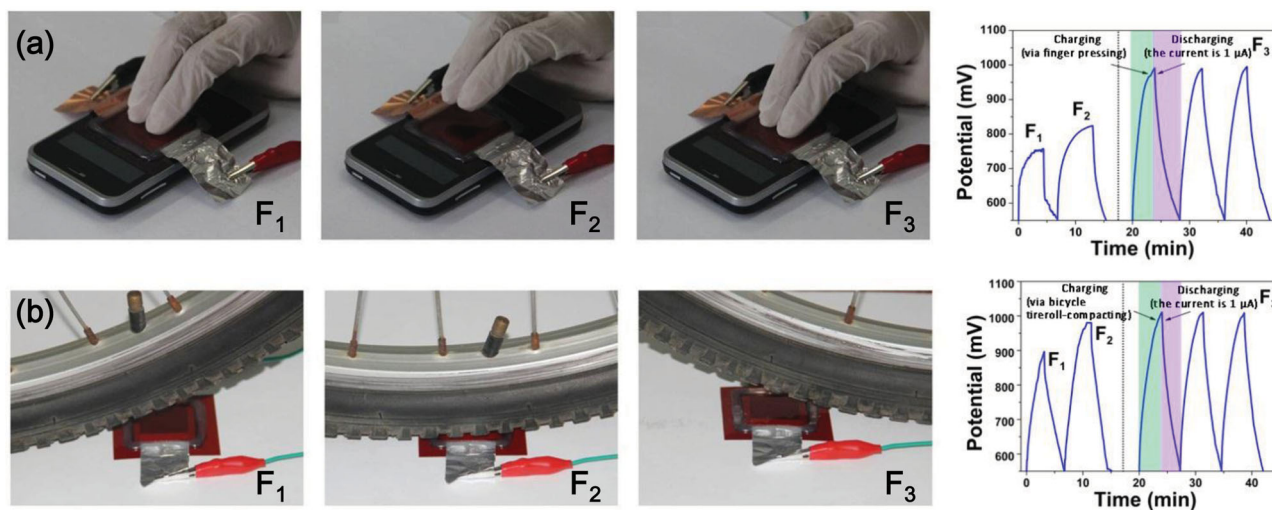

Figure 6. a,b) A flexible SCPC can conveniently be charged by finger pressing and the rolling compaction of a bicycle tire. The discharge current is 1 μA.

enough strain for the flexible SCPC. As shown in Figure 6a, under finger pressing at a frequency of ca. 1 Hz ($F_1 < F_2 < F_3$), the flexible SCPC can be charged to 757, 824, and 990 mV, respectively. The flexible SCPC can also be charged by the compaction caused by the rolling of a bicycle tire, as shown in Figure 6b. The SCPC can be charged to 896, 980, and 1010 mV in 240 s under deformation at ca. 1 Hz ($F_1 < F_2 < F_3$), respectively. These results should stimulate a research trend of flexible SCPCs that effectively harvest and store small amounts of mechanical energy in our living environment.

In summary, a flexible self-charging power cell (SCPC) is fabricated for the first time using graphene electrodes and Kapton shells, which directly converts mechanical energy into electrochemical energy. Such a device hybridizes a piezoelectric nanogenerator, a Li battery, and a power-management system, and can be directly used as a power source. Such a flexible structure can greatly avoid the waste of mechanical energy by the shells and electrodes in comparison to the previously demonstrated hard-shell SCPC. The flexible SCPC can be charged by the human body and by machine movement. Our results can facilitate the practical applications of SCPCs for harvesting and storing mechanical energy in our living environment.

Experimental Section

Graphene was synthesized via a hydrothermal route by using high-temperature pyrolysis. Firstly, 10 mL ethanol containing 2 g sodium was transferred into a Teflon-lined stainless steel autoclave and then kept at 220 °C for 72 h. The resulting white products were pyrolyzed at 960 °C for 35 s, and the graphene nanosheet was finally collected.

The anode of the flexible SCPC was a graphene:conductive carbon:binder mixture with a weight ratio of 8:1:1, pasted on Cu foil. The cathode was a $LiCoO_2$:conductive carbon:binder mixture with a weight ratio of 8:1:1, pasted on Al foil. The PVDF film (after polarization) with a thickness of ca. 100 μm was used as purchased without further treatment. The anode, cathode, and PVDF separator were filled with liquid electrolyte (1 m $LiPF_6$ in 1:1 ethylene carbonate: dimethyl carbonate) and finally sealed with ethylene vinyl acetate (EVA) between the Kapton boards.

The morphologies of graphene nanosheets were investigated by using a scanning electron microscope (SEM, JEOL JSM-6700F). The electrochemical performance of the flexible SCPC was evaluated by galvanostatic charge/discharge tests between 3 and 4.1 V at room temperature.

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