**Memristor-Integrated Voltage-Stabilizing Supercapacitor System**

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Recently, a great demand for high-performance multifunctional integrated systems has arisen for use in integrated electronics because of the maximum functionality of these integrated systems at minimized size. Considerable research efforts have been made to integrate different functional units into single multifunctional micro/nanosystems, such as solar cell-integrated photo-supercapacitor,[1-4] solar cell-electrochromic smart windows,[5] hydrogen generation-supercapacitor,[6] and photodetector-supercapacitor nanosystems.[7] etc. These indicated designed integrated systems can not only avoid some space and energy consumption form the external connection circuit but also achieve some new functionalities by incorporating different devices into single system.

As one of the most potential energy storage devices, supercapacitors have attracted increasing interest in the past few years owing to their high power density, long cycling life, and high energy efficiency.[8-12] However, one drawback associated with supercapacitors is that their voltage often significantly decreases once they begin to discharge as power sources, which greatly affects the smooth operation of the electronic/optoelectronics devices. To avoid this drawback, one should consider introducing voltage-stabilizing unit into supercapacitors. However, the up-to-date existing voltage-stabilizing units still possess several unsatisfying features, including redundant circuits, complicated and high cost procedures, etc, which makes it hard to integrate with supercapacitor to fulfill multifunctional demands at minimized scales. As the fourth circuit element, memristors have observable effects in resistance switching memory.[13,14] Considering the unique features of memristors, voltage-stabilizing characteristics may be fulfilled if one could integrate a memristor with a supercapacitor.

In this work, for the first time, we fulfilled a new voltage-stabilizing supercapacitor system by the integration of SnO$_2$-based memristor with PCBM-based supercapacitor. PCBM-based flexible supercapacitor was first fabricated by using the NIL technique, which delivered excellent cycling life, enhanced areal capacitance, and stable electrical stability under bending. Then, a memristor-integrated voltage-stabilizing supercapacitor was proposed, which facilitates a potential feasibility of functional relationship between the fundamental circuit-components (Figure S1, Supporting Information). Our work here opens up a new approach to fabricate new voltage-stabilizing systems and will bring a new boost for future electronics.

To fabricate the flexible supercapacitor with patterned electrodes, nanoimprint lithography (NIL) technique was applied. NIL stands out as a promising technology for high throughput and resolution nanoscale patterning, which has been introduced in various applications.[15-20] Beyond its fundamental nano-patterning interest, it is highly desired to develop this efficient and facile way to fabricate lightweight, flexible, and transparent electrodes for advanced energy-storage devices, especially supercapacitors.[21-31] The typical fabrication processes for the supercapacitors were illustrated in Figure 1a, which consists of five steps: (1) nanoimprint lithography (NIL), (2) sputtering, (3) spraying, (4) assembling, and (5) molding. In the NIL process, intermediate polymer stamp (IPS) films were pressed with Si mold to form the nanorod arrays after demolding. Interestingly, the as-prepared IPS films have outstanding transparent and flexible features (Figure 1b and Figure S2, S3, Supporting Information), indicating their great potentials in future transparent/stretchable electronics. The remarkably uniform nanorod arrays were verified by atomic force microscopy (AFM) measurement (Figure 1c). The 3D AFM image further shows that the height of the nanorods is about 200 nm (Figure 1d). Their corresponding nanopatterning is observed by scanning electron microscope (SEM) after sputtering Pt layer. The SEM images show the formation of orderly IPS nanorod arrays on a plane (Figure 1e and Figure S4) and their diameters is approximately 200 nm (Figure 1f).

Previously, PCBM ([6,6]-phenyl-C$_6$1-butyric acid methyl ester), a fullerene derivative, was widely applied in solar cells due to its high electron mobility, good solubility, and excellent phase separation. It is expected that breakthrough advancements could be gained in novel energy storage units by combining PCBM active materials with the NIL technique for future electronics. Here, our nanopatterned PCBM/PT/IPS electrodes were fabricated by coat-spraying method. The optical image of the PCBM solution is shown in Figure 1g (The detailed description of its fabrication process is stated in Experimental Section). It was observed that all the IPS nanorods are uniformly
covered with PCBM, as shown in Figure 1h. The diameter of the final regular rods with PCBM coating increased to about 400 nm, and the gap between these adjacent nanorods are filled with PCBM materials, which leads to a PCBM/IPS core/shell architecture as an electrode, as shown in Figure 1i. After the fabrication of the PCBM/IPS core/shell electrodes, two of the as-fabricated electrodes were assembled into an all-solid-state supercapacitor, as depicted in Figure 1j, which still keeps the features of excellent flexibility.

The capacitive features of the as-assembled flexible supercapacitor, which includes two PCBM/Pt/IPS composite electrodes, PVA/H₃PO₄ electrolyte, and carbon electrodes (Figure 2a), were demonstrated in Figure 2. The cyclic voltammograms (CV) of the flexible supercapacitor show a typical symmetrical rectangular shape at various scan rates of 20, 30, 50, 80, and 100 mV s⁻¹, which indicates their electrical double-layer capacitor features (Figure 2b) according to previous reports. The capacitance of the as-fabricated supercapacitors is associated with the accumulation of electrostatic charge in an electrochemical double layer formed at the PCBM/electrolyte interfaces. To better verify the advantages of the nanopatterning-based electrodes, the CV curves of a comparative supercapacitor with non-patterning electrodes was also measured (Figure 2c). It is observed that these electrodes have an extremely small area surrounded by CV curves at the corresponding scan rates, suggesting that their capacitive feature is worse than that of the PCBM/Pt/IPS nanopatterned electrodes. We can easily attribute it to the more enhanced surface area of the patterned PCBM/Pt/IPS electrodes in contrast to non-patterned electrodes. Figure 2d shows the charge/discharge curves of the patterned PCBM/Pt/IPS electrodes, and the corresponding calculated capacitances are 33, 28, 26, and 18 mF cm⁻² at 0.2, 0.5, 1.0, and 2.0 mA cm⁻², respectively, as summarized in Figure 2e.

The cyclic stability test of the devices is shown in Figure 2f. From the plot, after as long as 1000 cycles at 0.2 mA cm⁻², there is an only ≈6.4% drop in the capacitance of the device. Figure 2g demonstrates the first 4 charge/discharge curves, revealing the excellent cycling reproducibility of the patterned electrodes. Using our patterned PCBM/Pt/IPS films, the as-assembled highly flexible supercapacitor devices may find many potential applications in next generation flexible electronics. Figure 2h shows the CV curves of the as-fabricated flexible supercapacitor device under different bending states with different bending curvatures (30, 25, and 20 mm). The three curves are nearly unchanged at different bending states, revealing that the electrical stability of the flexible device is hardly affected by external bending stress. Figure 2i shows the CV curves of the flexible devices after bending for different cycles (50, 100, and 200 bending cycles) to further evaluate their corresponding folding endurance, which further verified the excellent mechanical flexibility of the as-fabricated flexible supercapacitor.

Figure 3 shows the characterizations of the memristors based on SnO₂ film, which was prepared from a sol-gel
The structure of the as-fabricated memristor was shown in Figure 3a, containing the active SnO$_2$ film on FTO glass, and the Ni electrode, which is measured on a probing station (Figure 3b). The crystallographic structure of the sol-gel synthesized product is analyzed by X-ray diffraction (XRD). All the diffraction peaks in Figure 3c can be readily indexed as SnO$_2$, which are well consistent with the values in the standard card (JCPDS Card No. 46–1088). The AFM images of the SnO$_2$ thin film in Figure 3d and Figure S5 reveals the extremely high smoothness of the SnO$_2$ film with the surface roughness (Rq) of 3.11 nm.

Figure 4a is the corresponding I–V curve of the memristor device in the voltage window of −5.4–5.4 V. From the curve, it can be observed that the I–V curve represents an inverse proportion between device voltage and resistance. To further confirm the unique properties of the memristors, many I–V relationships in several models, including $I \propto V^2$ for the space charge limited current (SCLC), $\ln(I) \propto \text{Sqrt}(V)$ for the Schottky emission, $\ln(I/V) \propto \text{Sqrt}(V)$ for the Poole–Frenkel (PF) emission, and $\ln(I/V^2) \propto 1/V$ for the Fowler-Nordheim tunneling, were used to fit the typical I–V results by Matlab software.$^{[37]}$ Compared to other models, the fitted value of PF model is best consistent with the measured value from the I–V curves, as shown in Figure 4b. The voltage region is dominated by the Poole-Frenkel (PF) emission at the interface between the electrodes and SnO$_2$ film. According to previous reports, the PF emission is a property that memristors have in high resistance state. With similar behavior, as a conclusion, our SnO$_2$ based device could be seen as a memristor.$^{[37]}$

As the fourth circuit element, memristors gained great research attention and till now, almost all of the researches are focused on the essential characteristics of memristors, while few work on the investigation of the functional relationship between memristor and the other passive elements (Resistor, Capacitor, and Inductor). To demonstrate the application of memristor as voltage-stabilizing unit, we designed a new memristor integrated supercapacitor system by the integration of the SnO$_2$-based memristor with the patterned PCBM-based supercapacitor. A photograph of the memristor-supercapacitor (M-S)
The integrated device was shown in Figure 5a. For the M-S integrated device, the supercapacitor (S) as a power source begun to work once it was charged to 1 V, as shown in Figure 5b. A stable discharging curve is obtained for the integrated device at about 0.8 V for as long as 200 s. and only about 0.11 V voltage drop was observed as shown in Figure 5c. While for the single supercapacitor (also shown in Figure 5b), once discharging, the voltage drops dramatically from 0.86 V to 0.3 V within the measured discharging time (200 s). Similar phenomena were also observed once both the devices, the integrated device and the single supercapacitor device, were charged to 1.5 V (Figure 5d, 5e). Importantly, the integrated device delivers an extremely low voltage-drop of only \( \sim 0.06 \) V in 200 s, revealing the possible application of the integrated device as stable energy unit for electronic and optoelectronic devices.

To explain the reason why the integrated M-S device delivered stable voltage during the discharging process, we draw the corresponding circuit schematics of both the single supercapacitor (Figure 5f) and the integrated M-S device (Figure 5g). In this figure, \( I_1, R_1, U_1, I_2, R_2, U_2, I_3, R_3, U_3 \) refer to electric current, resistance, and voltage of supercapacitor, memristor, and measured output-circuit, respectively. For the single supercapacitor system, the device as a power source begun to control the total circuit after it was fully charged. Since the electrical double-layer supercapacitors deliver quite rapid ion absorption and desorption in double layers at the interface between materials and electrolyte, leading to the inevitable on-going voltage decrease \( (U_3) \) of single supercapacitors without voltage-stabilizing components (Figure 5f). While considering an inverse relationship between \( U_3 \) and \( R_2 \) (Figure 4a), \( U_3 \) should gradually reduce for the discharging process of devices, which leads to rapid decrease of \( I_2 \) in the integrated M-S system (Figure 5g). According to the circuit principle: \( I_1 = I_2 + I_3 \). Here, lower electric current \( (I_2) \) derived from lower voltage \( (U_3) \) may cause more compensation for external output circuit \( (I_3) \). Finally, the synergistic effects of integrated devices can enable \( U_3 \) to smoothly keep almost constant. Therefore, memristor presented here plays a key role in circuit equilibration and regulation, which facilitates the realization of voltage-stabilizing characteristic. All these results indicate that it is a stirring breakthrough for future electronics: such a simplified voltage-stabilizing circuit formed with two fundamental passive elements (memristor and capacitor).

To demonstrate the real application of the integrated M-S system as stabilized energy units, we attempted to control commercial red LED by using the as-designed M–S system. From Figure 6a–c, for single a supercapacitor, it can be observed that the brightness of a lighten LED decreased very fast and then even fully disappeared within 100 s during a continuous discharging process. While for the M–S integrated system with voltage-stabilizing ability, the LED was found to be still lightened after 100 s, as shown in Figure 6d–f. The results confirm the voltage stabilizing features of our designed memristor-supercapacitor system.

In summary, we designed a new memristor-integrated supercapacitor system with voltage-stabilizing features. The supercapacitor used in the system was fabricated by the nano-imprint lithography process with the features of excellent cycle...
life, enhanced capacitance, and outstanding electrical stability under bending. Integrating the supercapacitor with a SnO\textsubscript{2}-based memristor, the final integrated system delivered obvious voltage-stabilizing effects as confirmed from both the circuit analyses and the display demonstration. Our work demonstrates the successful integration between the two basic circuit elements (capacitor and memristor) to fulfill new functions. By design of flexible memristor and reducing the size of both the memristor and the supercapacitor, the fully flexible memristor-supercapacitor may find real applications in current micro/nanoelectronics fields.

**Experimental Section**

**Fabrication of NIL-Based PCBM/Pt/IPS Electrodes for Supercapacitors:**

The cleaned intermediate polymer stamp (IPS) film was heated at 155 °C and then pressed by a patterned Si mold by nanoimprint lithography (NIL) technique (Etre3 Nano Imprinter) to obtain resulting nanorod arrays film. A Pt layer was sputtered onto this IPS thin film by using a precision etching coating system (PECS), Gatan, Model 682. In addition, 5 mg PCBM, [6, 6]-phenyl-C\textsubscript{61}-butyric acid methyl ester, was dissolved in 1 mL o-dichlorobenzene solution under continuous stirring for 12 h, and then the mixture was spin-coated onto IPS/Pt thin film at 2000 rpm for 60 s (KW-4A spin coater). After drying at 50 °C in vacuum oven, PCBM/Pt/IPS thin film electrodes were finally fabricated.

**Figure 5.** The voltage-stabilizing properties of the supercapacitor-memristor integrated devices. a) The optical image of the integrated circuit in parallel. The discharging curves of the integrated devices from b,c) 1 V and d,e) 1.5 V, respectively. f,g) In addition, the working analysis of supercapacitor and supercapacitor-memristor circuits, respectively, is shown.

**Figure 6.** Display comparison of the single and integrated systems. A red LED driven by a–c) supercapacitor, and d–f) supercapacitor-memristor systems, respectively.
Preparation of the Ni/SnO₂/FTO Memristor Devices: SnO₂ thin film was fabricated by sol-gel method. Briefly, SnCl₄·5H₂O was dissolved in absolute ethanol. The solution was transferred into a three flasks and then heated at 30 °C for 12 h under stirring. The aqueous SnO₂ solution was spin-coated on the FTO glass, and then the film was baked on the hot plate at 130 °C for 10 min. Finally, the samples were annealing in the furnace at 560 °C for 3 h. For electrical measurement, Ni top electrodes were deposited on SnO₂ films by DC magnetron sputtering using a metal shadow mask.

Material Characterization: The morphology was investigated by field-emission scanning electron microscope (FESEM, FEI Sirion 200). The phase of the products was identified using a X-ray diffraction (XRD) diffractometer (X'Pert PRO, PANalytical B.V., Holland) with Cu Kα irradiation (λ= 1.5406 Å).

Device Assembly: The flexible supercapacitors were both composed of a sandwiched structure with two patterned PCB-coated IFS films and a layer of PVA/H₃PO₄ solid electrolyte. Then, the obtained PCB-based supercapacitor was integrated with an above Ni/SnO₂/FTO memristor to form a voltage-stabilizing circuit. Performance Measurement: The I–V curve of memristors was measured by semiconductor characteristic measurement system (Keithley 4200 SCS) at room temperature in ambient condition. The self-discharging curves of the integrated devices were performed on the electrochemical station (CHI 760D).

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

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