Solution-Processed Polymer Thin-Film Memristors with an Electrochromic Feature and Frequency-Dependent Synaptic Plasticity

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Emerging organic synaptic devices are promising in exploring soft and biocompatible neuromorphic computing systems. By means of a simple and low-cost solution process, the polymer thin-film memristors are designed and characterized. The polymer memristors have a bilayer structure composed of an ion-rich semiconducting layer and an ion-collecting conducting layer, where the ion redistribution depending on device operation history has an impact on carrier concentration and results in the memristive characteristics. A visible electrochromic feature is observed during the electrical measurements, supporting the proposed Li$^+$ ion drift/diffusion mechanism. The polymer memristors show the continuous and reversible conductivity tuning with a temporary memory effect, which enables the successful emulation of the frequency-dependent synaptic plasticity. The polymer thin-film memristors may offer a strategy for developing building blocks of organic neuromorphic circuits.

1. Introduction

Electrically driven synaptic devices have shown promise for constructing brain-inspired neuromorphic systems through basic hardware implementation. [1–3] Besides extensively investigated inorganic counterparts such as oxide-based memristors, [4–11] organic synaptic devices are increasingly attractive as well, [12–16] benefiting from their superior compatibility to biological interfaces, soft substrates, and low-cost/low-temperature processing. To mimic the synaptic plasticity in the brain that may lay a foundation of learning, organic synaptic devices should possess continuously variable states with appropriate state retention. Furthermore, the state change in response to action potentials should be frequency-dependent rather than intensity-dependent, according to the spike-rate-dependent plasticity (SRDP) and spike-timing-dependent plasticity (STDP) in biological synapses. [17–19] The effective approaches to the device characteristics often involve the mechanisms of cumulative charge trapping/doping and electrochemical redox reaction in organic active layers. [20–24] In particular, a nonstochastic and reversible mechanism is desired to realize the analog-type device modulation in a controlled manner. Thus, efforts on structure design and fundamental understanding of organic synaptic devices are still needed to address the aforementioned challenges.

Herein, a bilayer thin-film structure with solution-processed polymers is used to achieve the organic memristors, in which the conductivity tuning is continuous and reversible. The bottom conducting layer of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) serves as the temporary reservoir of abundant inflow ions, which is confirmed by the visible electrochromic phenomenon. The conductivity of the top poly(3-hexylthiophene-2,5-diyl) (P3HT) semiconducting layer can then be modulated by the ion redistribution. The current changes in the polymer thin-film memristors resemble the synaptic potentiation and depression, and it is demonstrated that this synaptic plasticity is strongly dependent on the frequency of voltage pulses. The results indicate that the polymer thin-film memristors could be fundamental elements for designing and building organic neuromorphic circuits.

2. Results and Discussion

The structure illustration of the polymer thin-film memristors is shown in Figure 1a, where the bilayer active film consists of a LiClO$_4$-doped P3HT (P3HT:LiClO$_4$) layer on top and a PEDOT:PSS layer on the bottom. Both the polymer layers are deposited by a simple and low-cost solution process. The embedding of LiClO$_4$ in the P3HT layer is to provide a number of mobile Li$^+$ ions, which can drift under an external electric field and accordingly change the device state. In the electrical measurements, voltage is applied to the top electrode of inert Au, and the bottom electrode of heavily doped Si is kept grounded. Figure 1b shows the current–voltage (I–V) characteristics of a typical polymer thin-film memristor with multiple cyclic scans. An apparent pinched hysteresis loop, as a fingerprint of
memristors\cite{4,25} is clearly present. The current varies in a continuous fashion depending on the voltage polarity, and the $I$–$V$ hysteresis loop is well repeatable upon 12 times scans, as demonstrated in Figure 1b. The memristive behavior is highly reproducible in 378 devices fabricated on 42 substrates in total, and the device-to-device variance is small. An example for nine bilayer polymer thin-film memristors fabricated on the same Si substrate is shown in Figure S1, Supporting Information.

To elucidate the working mechanism of the polymer thin-film memristors, two control devices are fabricated and characterized. First, as demonstrated in Figure 2a, the LiClO$_4$-free device consisting of only P3HT and PEDOT:PSS does not show any $I$–$V$ hysteresis loop. Second, the hysteresis is also absent in the single-layer (P3HT:LiClO$_4$) device without PEDOT:PSS (Figure S2, Supporting Information). Therefore, both LiClO$_4$ and PEDOT:PSS play critical roles, and a physical model based on the ion inflow/outflow from the PEDOT:PSS layer is proposed in the following to interpret the memristive characteristics of the polymer memristors.

As the P3HT:LiClO$_4$ and PEDOT:PSS layers are stacked in series, the resistance of the semiconducting P3HT:LiClO$_4$ layer is dominant, in contrast to that of the conducting PEDOT:PSS layer. In other words, the current is sensitive to the conductivity change in P3HT:LiClO$_4$ rather than in PEDOT:PSS. Furthermore, although Li$^+$ and ClO$_4^{-}$ ions are uniformly distributed in P3HT at the initial state, Li$^+$ ions are much easier to drift under an external electric field due to their small size compared with ClO$_4^{-}$ ones. As shown in Figure 1c, upon applying low positive voltage on the Au electrode at device state ②, Li$^+$ ions in the P3HT:LiClO$_4$ layer start to drift into the PEDOT:PSS layer. As a consequence, the following electrochemical reactions may occur to maintain the electroneutrality in the polymer layers\cite{26–29}

\begin{align}
\text{PEDOT}^+ + \text{PSS}^- + \text{Li}^+ + h^+ &\leftrightarrow \text{PEDOT}^0 + \text{Li}^+ + \text{PSS}^- \\
\text{P3HT}^0 + \text{ClO}_4^- + h^+ &\leftrightarrow \text{P3HT}^+ + \text{ClO}_4^- 
\end{align}

The inflow of Li$^+$ ions will induce a decrease in PEDOT$^+$ and thus reduce the hole concentration in PEDOT:PSS. However, the reduction in hole concentration is minor compared with a great number of holes in the conducting PEDOT:PSS layer, such that its conductivity does not change significantly. On the other hand, the outflow of Li$^+$ ions will allow the generation of holes in P3HT
ions. Consequently, the device conductivity can be modulated by means of the ion redistribution.

Significantly, the occurrence of Equation (1) is often accompanied by an electrochromic phenomenon,\cite{26,27,30} which is not visible in the specific device region owing to the block of the Au electrode on top. However, as shown in Figure 1d, a prominent electrochromic feature surrounding the Au electrode is observed at device state @ with applying relatively high positive voltage. This may result from the lateral diffusion of \( \text{Li}^+ \) ions, as a result of the excessive ion inflow and accumulation in PEDOT:PSS underneath the Au electrode. Meanwhile, the current is increased rapidly and results in a counterclockwise \( I-V \) hysteresis under positive voltage, arising from the significant hole generation in P3HT based on Equation (2). The surrounding electrochromic area is expanding upon scanning high positive voltages, and it will shrink when high negative voltage is applied at device state @ (Figure 1e). In this case, a clockwise \( I-V \) hysteresis appears under negative voltage, as \( \text{Li}^+ \) ions tend to return to the P3HT:LiClO\(_4\) layer, and therefore, holes in P3HT are reduced. The electrochromic feature is eventually vanished after returning to zero voltage, which is demonstrated at device state @ in Figure 1f. As a straightforward evidence, a video in situ recording the evolution of the electrochromic feature is provided (Video 1 in Supporting Information). The aforementioned electrochromic phenomenon is consistent with the consideration that the ion redistribution in the polymer thin film should be a reversible and history-dependent process. As schematically shown in Figure 1a, the interspace among adjacent devices is much larger than the surrounding electrochromic area, such that inter-device talk is not involved in the present case.

Figure 2a shows the ion concentration dependence of polymeric memristors, where the weight ratio of P3HT to LiClO\(_4\) is modified from 7:0 (without LiClO\(_4\)), 7:0.5 to 7:1. It is clear that the memristive characteristics are more pronounced with a higher concentration of LiClO\(_4\) in P3HT. However, the further increase in the LiClO\(_4\) content in P3HT may cause phase separation and reduce the interaction between LiClO\(_4\) and P3HT, which is adverse to the memristive characteristics. Thus, the weight ratio of 7:1 is around the optimal one. In addition, the memristive characteristics are also dependent on the voltage scanning range, as shown in Figure 2b. With increasing the voltage range from ±2 to ±7 V, the \( I-V \) hysteresis is strongly enhanced at both positive and negative voltage sides. These dependencies indicate the predominant function of the ion redistribution driven by an external electric field, in good agreement with the working mechanism discussed in the previous section.

The remarkable memristive characteristics of the polymer thin-film memristors allow to tune the device current in an analog fashion. Figure 3a shows the continual current increase upon applying multiple positive voltage scans (each from 0 to 5, and then back to 0 V). In contrast, the continual current decrease is present in Figure 3b when multiple negative voltage scans (each from 0 to −5, and then back to 0 V) are applied. Again, the electrochromic phenomena appear simultaneously with the current changes in Figure 3a,b, as demonstrated by Video 2 and Video 3 in the Supporting Information, respectively. These results further verify the validity of the proposed ion drift model.

For the short-term plasticity of biological synapses, the action potentials arriving at presynaptic membrane result in temporary accumulation of Ca\(^{2+}\) ions that can induce the release of neurotransmitters to modify the synaptic connectivity.\cite{31,32} Analogously, the \( \text{Li}^+ \) ion redistribution caused by voltage pulses can modulate the conductivity of the polymer thin-film memristors. For instance, as shown in Figure 3c, a train of positive/negative voltage pulses (5/−5 V, 10 ms) with an intermittent reading at 1 V lead to the excitatory/inhibitory current change, respectively. The profile of the reading current variation, with continuous and reversible characteristics, is very similar to the synaptic potentiation and depression. Moreover, although the \( \text{Li}^+ \) ion drift could generate multiple device states with a temporary memory effect, the spontaneous back diffusion of \( \text{Li}^+ \) ions will make the memristors return to their thermodynamically stable original state at power off. Such a degree of volatility is beneficial to mimic the frequency-dependent synaptic behaviors,\cite{33,34,35,36,37} which may form the basis of information transmission and processing in neurons.

![Figure 2](image-url)  
**Figure 2.** Ion concentration dependence and voltage range dependence of polymer memristors. a) Current–voltage characteristics of bilayer polymer thin-film memristors with different weight ratios of P3HT to LiClO\(_4\) (7:0.5 and 7:1) and without LiClO\(_4\) (7:0). Voltage scanning sequence is from 0 to 5, then to −5 and back to 0 V. b) Current–voltage characteristics of a bilayer polymer thin-film memristor (weight ratio of P3HT to LiClO\(_4\) is 7:1) measured in different voltage scanning ranges (from ±2 to ±7 V).

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The information provided here is a natural representation of the document's content, focusing on the key aspects of the research described, including the experimental setup, observations, and implications for biological synapses.
In biological synapses, high-frequency stimuli often cause the synaptic potentiation with an enhanced probability of neurotransmitter release, whereas the synaptic depression normally occurs in the case of low-frequency stimuli. Such frequency-dependent synaptic plasticity can be emulated by the polymer thin-film memristors, whose typical current responses to different frequencies of voltage pulses (5 V, 5 ms) are shown in Figure 4. In this measurement, the initial state is set between device states ① and ② in Figure 1, at which some Li\(^+\) ions are already injected from the P3HT:LiClO\(_4\) layer into the PEDOT:PSS one. For a relatively low frequency of 5 Hz, a gradual decrease in current corresponding to the synaptic depression (D) is observed. It is ascribed to that the back diffusion of Li\(^+\) ions in pulse interval has a stronger effect than the Li\(^+\) ion drift during pulse application. With raising the frequency, pulse interval is reduced, such that the effect of the Li\(^+\) ion drift becomes dominant and the current will turn to increase. Furthermore, the current enhancement should be more prominent for higher pulse frequency. The slow, moderate, and rapid increases in current for 10, 20, and 50 Hz are demonstrated in Figure 4, which can correspond to the weak potentiation (WP), moderate (P), and strong potentiation (SP), respectively. The frequency-dependent current variation is repeatable, and it is consistent with the emulation results of the paired-pulse facilitation (PPF) in artificial synapses, where the time interval between paired input pulses determines the final current enhancement.

Therefore, the polymer thin-film memristors have potential to be used for dealing with complex signal processing tasks. In addition, such organic devices have a simple structure based on the solution process, and their power consumption can be reduced by decreasing the device area and minimizing the active layer thickness.

3. Conclusion

In conclusion, the solution-processed polymer thin-film memristors are achieved by utilizing a bilayer structure of
This bilayer configuration allows the electrically driven ion redistribution to modify the device state in an analog form, which could be a general approach to make thin-film memristors. The memristive characteristics of the polymer memristors arise from the reversible Li$^+$ ion drift and its effect on the hole concentration in the P3HT layer. The working mechanism is supported by the in situ electrochromic feature that is considered to be also induced by the ion redistribution. Taking advantage of the device behaviors, the frequency-dependent synaptic plasticity, including synaptic depression and different levels of synaptic potentiation, is successfully emulated. The polymer thin-film memristors with the simple structure and easy processing may be utilized as a key component in organic-based networks toward soft neuromorphic computing systems.

4. Experimental Section

Device Fabrication: The polymer thin-film memristors were fabricated on n-type heavily doped Si wafers, which act as the bottom electrodes. The Si wafers were cleaned by ultrasonic bath in acetone and isopropanol, and then by ozone treatment for 15 min. PEDOT:PSS (Heraeus, 3 wt%) was spin-coated on Si at 3000 rpm for 40 s, followed by annealing at 120 °C for 10 min. On the other hand, LiClO$_4$·3H$_2$O (Aladdin, $M_w$ ≈ 160 g mol$^{-1}$) was dehydrated in vacuum at 120 °C for 24 h, and then was dissolved with P3HT (Rieke Metals, $M_w$ ≈ 36 kg mol$^{-1}$) at 7 mg mL$^{-1}$ in tetrahydrofuran. The mixing composition was modified by changing the weight ratio of P3HT to LiClO$_4$. The P3HT:LiClO$_4$ solution was spin-coated onto the PEDOT:PSS layer at 6000 rpm for 40 s, followed by annealing at 75 °C for 30 min in a glove box. In the end, the Au top electrodes ($500 \times 500 \mu$m) of about 50 nm were deposited on the polymer surface by thermal evaporation in high vacuum.

Device Characterization: The electrical characteristics of the polymer thin-film memristors were measured with a semiconductor parameter analyzer and a source meter (Keithley 4200 and 2461) that were wired to a high-vacuum probe station (Lake Shore). The thicknesses of the PEDOT:PSS and P3HT:LiClO$_4$ layers were estimated to be about 40 and 60 nm by atomic force microscopy, respectively. The photos and videos on the electrochromic feature were in situ recorded during the electrical measurements with an optical microscope connected to a display.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.
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