Tunable Synaptic Plasticity in Crystallized Conjugated Polymer Nanowire ArtificialSynapses

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In biological synapses, short-term plasticity is important for computation and signal transmission, whereas long-term plasticity is essential for memory formation. Comparably, designing a strategy that can easily tune the synaptic plasticity of artificial synapses can benefit constructing an artificial neural system, where synapses with different short-term plasticity (STP) and long-term plasticity (LTP) are required. Herein, a strategy is designed that can easily tune the plasticity of crystallized conjugated polymer nanowire-based synaptic transistors (STs) by low-temperature solvent engineering. Essential synaptic functions are achieved, such as excitatory postsynaptic current (EPSC), paired-pulse facilitation (PPF), spike-frequency-dependent plasticity (SFDP), spike-duration-dependent plasticity (SDDP) and spike-number-dependent plasticity (SNDP), and potentiation/depression. The balance between crystallinity and roughness is successfully adjusted by altering solvent compositions, and plasticity of the synaptic device is easily tuned between short term and long term. The evident transition from STP to LTP, good linearity and symmetry of potentiation and depression, and the broad dynamic working range of synaptic weight are achieved. This provides a facile way to tune synaptic plasticity at low temperatures and is applicable to future organic and flexible artificial nervous systems.

The artificial synapse is an important neuromorphic device, that has not only been used in brain-inspired computing but also in artificial sensory systems. Unlike the “0/1”-based binary memory system, artificial neural networks can emulate both the structural and functional brain systems during decision-making and learning processes to develop next-generation neuromorphic computing. Artificial synapses receive, process, and transmit signals from tactile,[7–9] visual,[10,11] and auditory[12] senses in the human perception system, that could be possibly applied to humanoid robots and intelligent prosthesis.

Recently, great efforts have been made to modulate intrinsic synaptic plasticity in a fixed material and device structure to meet different application requirements. Lee and coworkers prepared 2D, quasi-2D, and 3D halide perovskite artificial synapses and studied dimensionality-dependent plasticity. The retention time of postsynaptic currents can be controlled by adjusting the dimensionality of the perovskite layer. Chen and coworkers demonstrated a synaptic–property–tunable synaptic transistor (ST) using a single intrinsic semiconducting polymer that emulates universal synaptic behaviors of both brain and peripheral nervous systems by simply adjusting the annealing temperature. Wan and coworkers investigated pH-dependent synaptic responses, the devices show an enhanced sensitivity in terms of the relative gain of excitatory postsynaptic current (EPSC) amplitude between pH = 4 and pH = 10, wherein the optimizing device is promising for low-power neuromorphic sensing systems. Chen and coworkers demonstrated a floating-gate organic ST capable of accelerated learning ability induced by temperature-facilitated modulation of synaptic plasticity, which can reduce energy consumption and promote the application of devices in a different environment. However, high annealing temperatures and severe pH conditions are sometimes not beneficial to organic electronics, which is usually anticipated for flexible applications. A new strategy that uses a mild condition but can easily tune the intrinsic plasticity is desired.

Organic materials have tunable properties by easy modification of chemical and physical structures. In addition, it is compatible with the solution process that enables facile and scalable fabrication. Therefore, many efforts have been made to fabricate artificial synapses based on organic materials. However, most of them are based on small molecules. Conjugated polymer thin films possess large free volume to modulate ion migration, and thus we choose conjugated polymer thin films to tune synaptic plasticity by adjusting their microarchitecture.

Here, we design a strategy that can easily tune the plasticity of crystallized conjugated polymer nanowire-based STs by low-temperature solvent engineering. Also, we systematically study...
the influence of crystallinity and roughness on essential synaptic functions, such as EPSC, paired-pulse facilitation (PPF), spike-frequency-dependent plasticity (SFDP), spike-duration-dependent plasticity (SDDP) and spike-number-dependent plasticity (SNDP), and potentiation/depression. A clear transition from short-term plasticity (STP) to long-term plasticity (LTP), good linearity and symmetry of potentiation and depression, and the broad dynamic working range of synaptic weight were achieved. This provides a principle for optimizing the synaptic plasticity performance for different applications such as neuromorphic computing and artificial nervous systems.

We fabricated a series of different crystallized poly(3-hexylthiophene) (P3HT) films by low-temperature solvent engineering (Experimental Section, Supporting Information). Typically, changing the combination of good and poor solvents can alter the self-assembly of polymer chains. For example, in good solvents like dichloromethane (DCM), P3HT chains aggregate and form nanowires (NWs).

We dissolved P3HT in mixed solutions with different CB and DCM ratios (CB:DCM = 100:0, 75:25, 50:50, and 25:75, volume fraction). To completely dissolve P3HT, the solution was heated at 60 °C. After aging for 5 days, these solutions with different ratios were spin coated on SiO2/Si substrates and glass substrates. We systematically investigated their assembly using atomic force microscopy (AFM), scanning electron microscopy (SEM), grazing-incidence X-ray diffraction (GIXD), and ultraviolet-visible spectroscopy (UV–vis) (Figure 1, 2).

SEM and AFM images show the morphology of P3HT NWs, each NW has a typical height of 5–6 nm, width of 20–45 nm, and lengths greater than micrometers (Figure 1 and Figure S1, Supporting Information). As the proportion of DCM increased, the NWs become denser and slender. A highly crystalline P3HT NW enables the formation of a continuous network. The RMS surface roughness values of the films are 0.70, 1.32, 3.56, and 5.99 nm for 100:0, 75:25, 50:50, and 25:75 of CB:DCM volume ratios.

To compare the crystallinity, we recorded GIXD profiles for all P3HT NW-based thin films (Figure 2a–d). The GIXD pattern collected using a 2D detector reveals structural information of out-of-plane ordering (vertical direction, $q_y$) and in-plane ordering (horizontal direction, $q_x$) (Figure 2e). All the 2D GIXD patterns showing the (100) peak is along $q_y$, whereas the (010) peak is along $q_x$, indicating P3HT with predominantly edge-on orientation. There is a diffuse isotropic ring in the GIXD patterns (Figure 2a), which shows very broad peaks in the line profiles at $q_y$ (Figure 2f), arising from the disordered alkyl chains of P3HT. More clearly developed (h00) reflections imply higher crystallinity (Figure 2c,d). The (100) peaks in the out-of-plane direction shifted to higher $q_y$ values, whereas the (010) peak disappeared, indicating a closer packing of the P3HT chains (Figure 2f). The (010) intensity of the in-plane reflection gradually increased, indicating improved π–π interchain stacking (Figure 2g). Overall, the GIXD results suggested that the crystallinity of the P3HT NW films increased as the ratios of the marginal solvent increased, which facilitated charge carrier transport in the channel.

The molecular ordering in the P3HT films with different ratios of CB:DCM was further characterized by UV–vis absorption spectra (Figure 2h). All of the absorption spectra are normalized to their maximum values to better compare the influence of crystallinity. The absorption spectrum exhibits vibronic features at 535, 560, and 610 nm. As the proportion of DCM increased, the absorption spectrum began to exhibit an evidently increased absorption peak at 610 nm, corresponding to enhanced conjugation.

To study the influence of crystallinity and roughness on device performance, we fabricated STs based on a series of different NW thin films (Figure 3a). We denoted these STs as ST0, ST25, ST50, and ST75 in correspondence to CB:DCM = 100:0, 75:25, 50:50, and 25:75, volume fraction. These STs respond differently when emulating important functions of biological synapses.

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Figure 1. a–d) SEM images and e–h) AFM topographical images of P3HT films: spin coated from mixed CB/DCM solvents with different ratios of 100:0, 75:25, 50:50, and 25:75, respectively. (Scale bar: 1 μm).
A presynaptic spike (−4 V, 28 ms) applied on the ion gel and EPSC was recorded at a constant drain voltage of −0.02 V. Before the spike, anions and cations in the ion gel were distributed randomly. When a negative presynaptic spike was applied, anions accumulated at the ion gel/P3HT interface or injected into the P3HT to attract additional holes in the conductive channel to form EPSC. After the spike, the distribution of anions gradually returns to random, and the EPSC decays. The EPSC peak was 7.85, 8.19, 16.97, and 10.32 μA for ST0, ST25, ST50, and ST75, respectively (Figure 3b). Energy consumption was estimated as $V_D \times I \times t$, where $V_D$ is the drain voltage, $I$ is the peak value of the EPSC, and $t$ is the duration of spike. The energy consumptions of ST0, ST25, ST50, and ST75 are 4.4, 4.6, 9.5, and 5.8 nJ for a synaptic event, respectively. To systematically study the influence of crystallinity and roughness on synaptic plasticity, we adjusted the number, duration, and frequency of spikes to compare the response from different ST$n$. SFDP is considered to be an extended form of Hebbian learning and is related to learning, associative memory, and forgetting. Repeated synaptic spikes at varied frequencies (1, 2, 3, 6, and 13 Hz) were applied to the artificial synapse (Figure 3c). The spike-frequency-dependent postsynaptic currents were shown. SDDP could be utilized for designing duty cycles-coded algorithms for multiple bit storage and processing. SDDP was emulated using the P3HT NW synaptic devices (Figure 3e). Here, the duration of the spike varies from 28 to 215 ms, and EPSC increased with increasing duration. An increased number of spikes can mimic repeated rehearsal processes to modulate synaptic plasticity.

Figure 2. a–d) GIXD patterns for the crystallized P3HT-NW films as spin coated from mixed CB/DCM solvents at different ratios of 100:0 (pink), 75:25 (orange), 50:50 (green), and 25:75 (blue), respectively. e) Synchrotron X-rays are incident on the sample at an angle of 0.12°. The GIXD pattern collected on a 2D detector reveals structural information of f) out-of-plane ordering (vertical direction, $q_z$) and g) in-plane ordering (horizontal direction, $q_{xy}$). h) UV–vis absorption spectra of aforementioned P3HT films are normalized at 560 nm. The absorption spectrum of P3HT exhibits characteristic peaks at 535, 560, and 610 nm. As the proportion of DCM increased, the absorption spectrum began to exhibit an evidently increased absorption peak at 610 and decreased absorption peak at 535 nm.
plasticity.\textsuperscript{12,13} SNDP was also observed in our artificial synapses (Figure 3g). As the number of spikes changed from 5 to 50, the amount of migrated TFSI/$C_0$ increased; thereby, EPSC increased. We plotted EPSC as a function of ST$_n$ (Figure 3d,f,h). There is a maximum point in the curve. EPSC increased first and then decreased, showing that EPSC is not only dependent on crystalinity but also relies on roughness. When the crystallinity of P3HT increased, the roughness also increased, which acts as counteractive factors to the current, and thus a balance between the crystallinity and roughness needs to be found to optimize the device (Figure 3i).

As a typical type of STP, PPF function was emulated using our device (Figure 4a). Two consecutive spikes ($-4\text{ V}, 28\text{ ms}$) with different time intervals ($28 \leq \Delta t \leq 486\text{ ms}$) were applied to the gate electrode. The PPF index of the ST decreased gradually as $\Delta t$ increased, analogous to the forgetting curve of a brain (Figure 4b).\textsuperscript{[33]}

Biological synapses with different STP and LTP depend on their roles and locations. In biology, the formation of long-term memory requires repeated rehearsal processes (Figure 4g). We applied a different number of stimuli to strengthen STP and calculated postsynaptic current ($\Delta PSC = EPSC - I_b$; $I_b$: current before applied spikes) to study the transition between STP and LTP. When increasing the number of spikes from 5 to 50, the current levels of ST0 and ST25 were enhanced, but they fall back to baseline in a short time (Figure 4c,d). In contrast, the retention $\Delta PSC$s of ST50 and ST75 can be more than 1 min, indicating the transition from STP to LTP (Figure 4e, f). This discipline can be explained by crystallinity. In high-crystallinity films, doped ions that are trapped cannot diffuse out easily after the spike is removed, so ST50 and ST75 need more time to fall back to initiate states. Therefore, it is easier to modulate the composition of mixed solvents to obtain ST for different applications. Artificial sensory systems are inclined to ST with STP for intelligent decision-making dynamics, whereas neuromorphic computing and pattern recognition prefer LTP for obtaining higher accuracy.\textsuperscript{[12]}

We applied 30 repeated negative ($-4\text{ V}, 50\text{ ms}$) and 30 positive (4 V, 50 ms) gate voltage spikes on ST$_n$ (Figure S2, Supporting Information). The synaptic currents of ST50 show the best linearity which benefits learning accuracy in neuromorphic computing networks.\textsuperscript{[34,35]} We further improve the symmetry of currents by reducing the depressing voltage (2 V, 50 ms) (Figure 4h). ST50 has well-distinguished 30 states with a broad dynamic range ($\approx 40\text{ }\mu A$ change in current) compared with other devices.
In conclusion, we demonstrated a series of crystallized P3HT NW STs, tuning their plasticity by low-temperature solvent engineering. Essential synaptic functions have been emulated, such as EPSC, PPF, SDDP, SNDP, potentiation/depression, and the transition from STP to LTP. We systematically studied the balancing effect of crystallinity and roughness on synaptic plasticity. The tunable synaptic plasticity between the short term and long term was easily realized on crystallized P3HT NW artificial synapses by adjusting the compositions of the cosolvent. The optimized performance of the synaptic device with a clear

Figure 4. a,b) PPF and PPF index (\(A_2/A_1 \times 100\%\)) triggered by two successive pulses with various time intervals (28 ≤ \(\Delta t\) ≤ 486 ms). c–f) The retention \(\Delta PSCs\) of STn were enhanced as the spiking number increased from 5, 10, 20, 30, to 50. ST0 and ST25 exhibit STP, whereas ST50 and ST75 exhibit the transition from STP to LTP. g) Schematic of rehearsal memory process in biology. h) Synaptic potentiation and depression of STn triggered by a series of repeated negative (−4 V, 50 ms) and positive (2 V, 50 ms) gate voltage pulses.
transition from STP to LTP, good linearity and the symmetry of potentiation and depression, and the broad dynamic working range of synaptic weight was achieved. The low-temperature process provides a strategy to modify short-term and long-term synaptic plasticity and is promising for use in organic and flexible neuromorphic electronics.

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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