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Keywords: Spatiotemporal Information, Intelligent Neuromorphic Systems, Self-Threshold Design, Artificial Axons, Efficient Neural-signal Analysis

Posted Date: December 2nd, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-114838/v1>

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Self-Adaptive Spike Voltage-dependent Plasticity Emulated by a Metalloporphyrin-Based Memristor

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By threshold-regulated neural firing and synaptic weight updates in biological neuron–synapse combinations, neural systems can selectively and autonomously encode and process spatiotemporal information. Emulating such an exquisite biological process in electronic devices is a fundamental step toward realizing intelligent neuromorphic systems with self-adaptivity, energy-efficient in-situ edge/parallel computing, and probabilistic inference. Here we report a self-threshold design of prototype artificial axons based on metalloporphyrin, a molecular medium that allows dual electronic/ionic migration in hybrid heterojunction oxide memristors. Threshold behaviors in biological neurons are emulated by introducing metalloporphyrin into alumina-oxide memristors. We show that the memristor achieves smooth, gradual conductive transitions. As a unique feature of such a hybrid system, the endurable current-voltage characteristics of the memristor can be enhanced by altering the metal center to achieve the desired metal–oxygen bonding energy and oxygen migration dynamics. The spike voltage-dependent plasticity is recorded with a positive threshold voltage stemming from the interfacial counterbalance between the vacancy-induced Coulomb force and the external electric field. We further build memristive arrays that directly emulate the self-adaptive and signal-filtering function of the human visual system. These results suggest that the metalloporphyrin platform offers vast opportunities for implementing efficient neural-signal analysis in neuromorphic hardware.

Spike-time-dependent plasticity in neuron-synapse assemblies is essential for cloning human consciousness in artificial neural networks. The fundamental features of spike plasticity are history-dependent spatiotemporal correlation^{1,2}, probability inference³, and in-situ analog–digital mixed-signal processing^{4–7}. To unlock the von Neumann bottleneck of neuromorphic computing, synaptic plasticity must be faithfully replicated in artificial synapses. Spike-rate-dependent plasticity (SRDP), the fundamental mode of Hebbian plasticity in learning mechanisms, has thus far been emulated in various artificial synapses based on Chua’s memristor concept^{8,9}. Another paradigm is spike-timing-dependent plasticity (STDP), which has been achieved by training oxide memristors on events with variable time intervals^{10,11}.

Despite vast progress, the physical processes in neuromorphic hardware significantly differ from those in actual synapses. These differences limit the fidelity and variety of desired synaptic functions. Especially, spike plasticity in neuron–synapse links is based on stimulation-generated action potentials. Physiologically, action potentials are generated by voltage-gated K^+/Na^+ channels, which in turn modulate Ca^{2+} channels that change the weights of synapses¹². Emulating the threshold-regulated plasticity, namely, the spike voltage-dependent plasticity (SVDP), is the inevitable direction of future brain-like computational systems^{13–15}. For example, SVDP would benefit development of artificial synaptic devices for more realistic neuromorphic visual systems that automatically eliminate background information through an adaptive noise-filtering mechanism¹⁶. However, achieving such threshold-regulated behaviors by artificial ionic channels in the vertical mode, where a precise ionic shuttle determines the smart selectivity of spiking events^{17–19}, has been an insurmountable task.

To achieve threshold-regulated plasticity, the voltage-gated ionic migration dynamics with dominant activation energy must be created in multilayered devices. Oxygen ions in oxide memristive devices are an ideal ionic source, as their activation energy can be tuned by changing vacancy ratios²⁰. They also provide insights into hemoglobin in red blood cells, which transports oxygen along the network of capillaries vasculatures into deep tissues of various organs^{21,22} (Fig. 1a). Such regular processes rely on metalloporphyrin (MTPP), a molecule with an iron-coordination center mounted on a planar ring, which reversibly binds oxygen via the coordination bond²³.

Inspired by these biological events, we reason that MTPPs with dual functionalities (electronic activity and ionic migration) could potentially be the molecular media for implementing adaptable ionic dynamics in memristors. Herein, we report a hybrid heterojunction of MTPP/oxide that facilitates the external field sensitivity of ionic responsiveness and enables artificial synapses with a

non-zero threshold voltage property. We show that this unipolar plasticity fundamentally differs from SRDP and STDP, and allows a potentiation voltage at 10 V and a depression voltage at 4 V. By programming different positive-voltage spikes at fixed frequencies and time intervals (Fig. 1b), we achieved neuromorphic systems with a self-adaptive signal-filtering functionality resembling that of human visual recognition systems.

The proof-of-concept memristive devices are configured as ITO/ZnTPP (~25 nm)/AlO_x (~7 nm)/Al (Fig. 1c, d). The non-stoichiometric AlO_x layer with oxygen vacancies is the reservoir of oxygen ions (O²⁻), while the ZnTPP layer adjusts the ionic oxygen migration. As indicated by the energy diagram (Supplementary Fig. 1), the device preferentially transports holes. In this device configuration, the ZnTPP layer is expected to act as a *p*-type active molecular framework that modulates the conduction of mixed O²⁻ ions and electrons. The ion redistribution triggers memristive switching^{24,25}. Over the voltage range from +10 to -10 V, the current-voltage (*I-V*) curve of the device showed a typical “figure-8” pinched hysteresis loop (Fig. 2a), whereas no hysteresis appeared in the cyclic sweeping curves of the ITO/ZnTPP/Al device (Supplementary Fig. 2). Judging from the gradually changing conductive states of hysteresis loops, the semiconducting characteristics in the ZnTPP/AlO_x device are regulated by ionic movement (in contrast to local filamentary-determined conduction in insulators). The potentiation and depression behaviors were examined in bipolar sweeping mode (Fig. 2b, 10 cycles in the 0→+10 V range scanned at 0.01 V/s, followed by 10 cycles in the 0→-10 V range scanned at 0.01 V/s). The ultimate currents of the positive and negative sweep cycles were markedly variable, being enhanced by approximately 270–778 μA and suppressed by -80 to -10 μA. The negative differential resistance peaked at -6.7 V during the first RESET sweep.

The *I-V* characteristics were further investigated by repeating low-voltage sweep cycles of 0 ↔ 4 V/0 ↔ -4 V (Fig. 2c). In the positive and negative directions, hysteresis loops appeared with ultimate currents decreasing approximately from 3.8–3.0 μA and from -2.00 to -0.96 μA, respectively, indicating that the low voltage caused a continuous transition into a higher resistance state. Therefore, the potentiation and depression in ZnTPP/AlO_x memristors can be selectively operated at a unipolar voltage (e.g., 10 V for potentiation and 4 V for depression; see Fig. 2d, e). This voltage threshold-regulated plasticity can be defined as SVDP. Unlike other forms of synaptic plasticity, such as SRDP and STDP, SVDP can be regarded as a relatively independent function of signal processing under a fixed timing interval and rate frequency. In this sense, it resembles the action potential of a neuron and synaptic plasticity under the mechanism of voltage-gated ionic channels. The voltage-threshold feature of the ZnTPP/AlO_x device might also realize advanced computing features such as parallel implementation, adaptivity, and probability inference. In addition, the smooth *I-V* curves were highly

repeatable (Supplementary Fig. 1), suggesting that hybrid ZnTPP/AlO_x is a suitable model for advanced neuromorphic computing.

To confirm the SVDP behaviors, we carried out additional measurements in biasing modes (Fig. 2f). The stimulus-response exhibited an inverse trend with a critical value of ~6–7 V. Bias stimuli above (10, 12, 13, or 14 V) and below (1, 2, 3, or 5 V) the critical value induced potentiation and depression, respectively. Hence, the devices can selectively perform potentiation and depression of input signals, resembling those of action potentials at neurons. These processes are reliable and reproducible, suggesting the robustness of this function in artificial neural hardware.

To shed light on the underlying mechanism of plasticity in the ZnTPP/AlO_x devices, we performed a series of structural and stoichiometric characterizations with theoretical simulations and device evaluations. The current and hysteresis areas were monotonically increasing functions of the device area ($5 \times 10^3 \mu\text{m}^2$ to $5 \times 10^5 \mu\text{m}^2$, Supplementary Fig. 3) and scanning speed (0.01–5 V/s, Supplementary Fig. 4). The current increased from ~74 to 1,500 μA in the high resistance state and from ~454 to 4,048 μA in the low resistance state, while the hysteresis area increased from ~54.9 to 2.0 $\text{V}\mu\text{A}/\text{cm}^2$. These results suggest that device behaviors with the SVDP feature are dominated by homogeneous ionic migration rather than by local filamentary conduction²⁶. Conductive filaments can also be excluded by the cross-sectional TEM images and X-ray spectroscopy (STEM-EDX) analyses of the memristor devices (Fig. 3a, c; Supplementary Figs. 5 and 6). When supplied with +7 V, the oxygen component in ZnTPP/AlO_x devices was redistributed in ZnTPP and AlO_x layers. Especially, the AlO_x thickness decreased from ~7 to ~5 nm, suggesting the partial reduction of Al³⁺ to Al and the departure of oxygen at the AlO_x/Al interface (Fig. 3a). As clarified in the line-scanning profile of O and Al (Fig. 3b), the O content (C) was markedly enriched throughout the ZnTPP film after applying the bias, either at the ZnTPP/ITO interface ($C_0/C_{+7} = 48.5/134.4$) or at the ZnTPP/AlO_x boundary ($C_0/C_{+7} = 51.5/61.4$), whereas the Al profile remained largely unchanged. This analysis visualized the pathway of the O²⁻ migration, directly supporting the scenario that plasticity in the ZnTPP/AlO_x devices arose from modulation of spatial O²⁻ distribution in the ZnTPP/AlO_x heterostructure.

The underlying interaction between ZnTPP molecules and mobile O²⁻ was further investigated by X-ray photoelectron spectroscopy (XPS). After the voltage application, the injection of O²⁻ into the ZnTPP layer was confirmed by the greatly enhanced O 1s signals at 530.85 and 531.21 eV (Fig. 3c; Supplementary Fig. 7), which were attributable to charged ionic oxygen species (O²⁻/O⁻) bonded with Zn²⁺ and free O²⁻ in the ZnTPP matrix, respectively^{27,28}. XPS analyses also revealed a blue shift (100 meV) in the Zn 2p spectrum after electrical stimulation (Fig. 3c), arising from the formation of

coordination bonds between Zn^{2+} and O^{2-} . Coordination bonding with fixed Zn^{2+} sites can finely regulate the ion distribution and migration, which are random in general memristive media²⁹⁻³¹.

To further investigate cation-anion interactions, we examined the metal-atom effect of MTPP (M = Zn/Ni/Co/Fe/2H) on the electric properties of the memristors (Supplementary Fig. 8). The metal effects of MTPPs are detailed in Tables S1 and S2. The initial conductance, conductance saturation, and change range strongly depended on the type of MTPP. As the different MTPPs possessed different M–O bonding energies, the results confirm the close correlation between O^{2-} movement and metal atoms. The ionic migration can thus be described as a hopping process through the MTPP molecular matrix, which consists of reversible M–O binding and dissociation of ionic oxygen from an MTPP, followed by association with another MTPP. This process also repeats in an iterative cycle (Fig. 3d). The basic kinetics of O^{2-} on the MTPP matrix can also be described by the Arrhenius equation $v = v_0 \exp[-(E_{M-O} - \varepsilon q a / 2) / k_B T]$, where E_{M-O} is the M–O bond energy, v is the escape frequency under the applied voltage, v_0 is the attempt-to-escape frequency, a denotes the average migration step, q is the charge of O^{2-} , k_B is the Boltzmann constant, and T is the temperature^{32,33}. The concentration and migration rate of O^{2-} are suppressed in the MTPP layer region with increasing M–O bond energy. Nevertheless, the two crucial parameters can be easily tuned by changing the metal centers and their layer thickness. Our results also confirmed the function of each layer as follows: the ZnTPP is the ionic/electronic media, while AlO_x is the ionic generation/migration layer that undergoes the electrochemical reaction.

Ionic migration in the ZnTPP matrix dramatically differs from that in AlO_x . In particular, both the energy and sites of binding and coordination environments differ between the two materials^{34,35}. The activation energy of O^{2-} hopping among the MTPPs is associated with the coordination bonds, and it is much lower than that of AlO_x , in which negative O^{2-} ions and positively charged oxygen vacancies (V_O) interact through Coulombic attraction. Because the ionic migration behaviors in ZnTPP and AlO_x layers are heterogeneous, the ZnTPP/ AlO_x interface presumably dictates the threshold voltage phenomena. Based on these findings, we hypothesized a molecular picture of the electric double layer with the in-situ stern-like binding layer between the O^{2-} and V_O , which exhibits the stimulus-responsive feature. This molecular description explains the robust unipolar plasticity occurring in ZnTPP/oxide hybrid devices (Fig. 3d; Supplementary Fig. 9). The main behavior of O^{2-} at the double electrical interface depends on whether the internal Coulomb attraction barrier of the ionic $\text{Al}^{3+}\text{--O}^{2-}$ pair can be overcome by the energy supplied by the external voltage field. When the applied bias exceeds the threshold voltage, the external electrical field provides enough power to split the $\text{Al}^{3+}\text{--O}^{2-}$ pair, initiating the migration of many O^{2-} ions from the edge of the stern-like binding layer. The

mobile ionic oxygens continuously raise the conductivity of the lowly conductive AlO_x and the $\text{ZnTPP}/\text{AlO}_x$ hetero-interface³⁶ (Fig. 3e; Supplementary Fig. 9). In contrast, when MTPP/oxide devices are operated below the critical field, a limited number of O^{2-} ions are freed from the edge of the slipping plane; moreover, within the main release area, the migration speed is quickly reduced by back-scanning owing to the dramatically reduced acceleration. Here, their drift is prevented by the insurmountable Coulomb force between Al^{3+} and O^{2-} (Fig. 3e). We concluded that Coulomb binding energy is the primary regulator of the ionic migration behavior under external energization.

To verify that our devices provide the building blocks for neuromorphic systems, we emulated key synaptic functions in paradigmatic ZnTPP memristors, which feature a wide range and high density of non-volatile intermediate states for multi-level computation applications. Certain synaptic functions such as short-term memory, long-term memory, learning–forgetting–relearning behaviors, and visual activity-dependent memory consolidation were emulated under specific programming stimuli (Supplementary Figs. 10-12). All synaptic responses remained smooth and exhibited gradual changes under long-term, repeated stimulation with different pulse numbers, intervals, and intensities, demonstrating the superiority of threshold voltage-dependent ion migration and consolidation for neuromorphic emulation.

The SVDP feature of MTPP/oxide memristors is potentially applicable to synaptic filtering in adaptive visual recognition and classification. During the perceptual signal processing of biological visual systems, the targeted optical information is converted into electrical signals when it is necessary to in-situ filter the irrelevant background artefacts by neuron–synapse network with the mechanisms of voltage threshold plasticity rather than SRDP and STDP³⁷. To demonstrate the superiority of the MTPP/oxide devices as building blocks for neuromorphic hardware, we conducted a validation study using three 8×8 ZnTPP memristor arrays. In our design, the yellow and violet arrays of the word “**Hi**” represent the input optical image and the memorized electrical pattern, respectively (Fig. 4a). Assuming sufficient conversion of the photonic signals into electrical signals, the graphic word “**Hi**” with and without background interference was repeatedly input to the memristor array, and the adaptive filtering capability of the array was evaluated. In the first commonly emulated case without background, only the memristor pixels corresponding to the word were input, along with stimulations ($V_{\text{target}} = 10/5$ V, $W = 100$ ms, $T_1 = 100$ ms, $T_2 = 300$ ms). In Case 2, a certain number of images was inputted, and the graphic word ‘**Hi**’ in case 2 was memorized and consolidated by a continuous increase of conductance G_{average} from 30.7 to 66.7 μS (Fig. 4b; Supplementary Fig. 13). Figure 4c presents two contrasting cases that affirm the superiority of SVDP in the signal-filtering process. Analogous to the biological visual nervous system, the array retained a residual impression of signals

that were presented earlier, mimicking the persistence of vision. Case 3 was another common emulation case, in which the noise filtering relied only on spontaneous decay. After 30 inputs, the impression level of the word was gradually enhanced from 31.5 to 59.6 μS ($S_{\text{target}} = 10/5 \text{ V}$, $W = 100 \text{ ms}$, $T_1 = 100 \text{ ms}$, $T_2 = 300 \text{ ms}$), whereas the noise pixels without filtering operation spontaneously relaxed to 18.4 μS . Finally, in Case 4, the target “**Hi**” pixels were operated with 30 identical inputs, but the noise pixels were applied with pulse stimuli ($S_{\text{noise}} = 6/5 \text{ V}$, $W = 100 \text{ ms}$, $T_1 = 100 \text{ ms}$, $T_2 = 300 \text{ ms}$, $N = 30$) (Supplementary Fig. 13). This case more closely represents the real biological situation than the other cases. The changing conductance values in each pixel are shown in Supplementary Figures 13 and 14. As expected, the impression of the word “**Hi**” in Case 4 was homoplastically changed from 32.1 to 58.0 μS , whereas the surrounding background information was considerably weakened to $\sim 7.4 \mu\text{S}$. Consequently, the signal-to-noise contrast ratio of Case 4 filtered by SVDP was approximately 8, which was much higher than in Case 3 without the low-voltage training operation.

In conclusion, we have demonstrated a new class of MTPP/oxide hybrid memristors with voltage-regulated potentiation and depression behavior. Coordination-regulated ionic dynamics in the memristors were unveiled by the STEM-EDS and XPS measurements. The coordination sites of MTPP molecules provide potential paths for oxygen migration, resulting in smooth, gradually changing memristive responses with durative characteristics. Additionally, the electrical properties of the memristors can be finely modulated by varying the metal constituents. As verified experimentally, these MTPP/oxide memristors exhibited short- and long-term plasticity, along with noise-filtering synaptic functions that have not been realized previously. Our artificial synapse elements provide a versatile platform for investigating the fundamental ionic dynamics in biological synapses. Moreover, they present a new building block for designing artificial neural network with adaptivity, fault-tolerance, and signal-filtering function.

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Acknowledgements: This research was supported by the National Basic Research Program of China (2014CB648300, 2015CB932200), National Natural Science Foundation of China (61475074, 21274064, 61136003, 21771135, 51933005), National Natural Science Funds for Excellent Young Scholar (21322402), Changjiang Scholars and Innovative Research Team in University (IRT_15R37), Natural Science Foundation of Jiangsu Province (BK20160088), the Qing Lan Project of Jiangsu Province, the Innovation Team of Talents in Six Fields of Jiangsu Province (XCL-CXTD-009), Singapore Ministry of Education (MOE2017-T2-2-110), Agency for Science, Technology and Research (A*STAR) (Grant NO. A1883c0011), National Research Foundation, Prime Minister's

Office, Singapore under the NRF Investigatorship Programme (Award No. NRF-NRFI05-2019-0003), Synergetic Innovation Center for Organic Electronics and Information Displays, Excellent Science and Technology Innovation Team of Jiangsu Higher Education Institutions (2013), and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD, YX03001).

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Author contributions: L.X., M.Y., X.L. and W.H. conceived and initiated the study. Z.W. and L.W. contributed to the fabrication of devices and electrical measurements. M.N. was responsible for STEM and EDX measurements. Q.L. performed theoretical calculation. R.J., H.L. and N.S. collected the data. Z.W., Y.W. and L.W. co-wrote the manuscript with contribution from L.B.. H.B., L.X., M. Y., X.L. and W.H. revised the manuscript, provided guidance, and directed the project.

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Competing interests: The authors declare that they have no competing interests.

Data and materials availability: All data and images are available in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

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Figure 1 | Concept of a molecular memristor with spike voltage-dependent plasticity (SVDP). **a**, Bio-inspired material selection. In vertebrate red blood cells, ferriporphyrin (a component of hemoglobin) reversibly binds to and delivers oxygen, allowing continuous oxygen delivery. **b**, Visual summary of plasticity in synapses and memristors. The proposed SVDP with unipolar plasticity allows selective depression or potentiation by programming different positive-voltage spikes with fixed frequency and different timing intervals. This process fundamentally differs from spike-rate-dependent plasticity and spike-timing-dependent plasticity. **c**, Schematic of ionic migration among MTTP molecules. M = Zn, Ni, Co, Fe-Cl, and 2H lead to ZnTPP, NiTPP, CoTPP, FeTPP-Cl, and TPP, respectively. **d**, Configuration of ITO/MTTP/ AlO_x /Al. The drift of internal oxygen ions (O^{2-}) dictates the switching behavior.

Figure 2 | Electrical characteristics of ZnTPP/AlO_x device. **a**, Typical $I-V$ curve showing a pinched hysteresis loop at positive and negative bias voltages. The voltage was swept from zero to 10 (–10) V, then back to zero. **b**, **c**, Hysteretic $I-V$ loops of the ZnTPP/AlO_x devices during 10 voltage-sweep cycles of $0 \rightarrow 10/-10 \text{ V} \rightarrow 0$ and $0 \rightarrow 4/-4 \text{ V} \rightarrow 0$, respectively. The device conductivity continuously increases (decreases) during the positive (negative) voltage sweeps. **d**, **e**, Conductance versus sweep cycles in potentiation and depression, respectively. **f**, Voltage-dependent conductive variations.

Figure 3 | STEM-EDX characterization and mechanism of the ZnTPP/AIO_x devices. a, STEM images and corresponding STEM-EDX elemental mapping of O (blue) in the virgin (i and iii) and energized (ii and iv) samples under a voltage bias of +7 V. **b**, Elemental line-scanning profiles from the Al to ITO sides [marked by white lines in **a** (i and ii)]. **c**, Typical high-resolution O 1s and Zn 2p XPS spectra. Data were collected from the pristine state after electrode polarization. **d**, Schematic of the proposed model. ZnTPP regulates memristive behavior by functioning as an ionic/electronic media. **e**, Schematic of O²⁻ redistribution under a weak (upper panel) and intense (bottom panel) external electric field.

Figure 4 | Proof-of-principle design of SVDP-based filtering with unipolar plasticity. **a**, Working process of visual recognition systems in the human brain. Photonic signals are converted into electric signals, and background or noise is efficiently filtered by the neuron–synapse network. **b**, Visualizations of the memorizing processes in an ideal case. **c**, Noise filtering with and without the SVDP mode. Each pixel represents a single memristor.

Figures

Figure 1

Concept of a molecular memristor with spike voltage-dependent plasticity (SVDP). **a**, Bio-inspired material selection. In vertebrate red blood cells, ferriporphyrin (a component of hemoglobin) reversibly binds to and delivers oxygen, allowing continuous oxygen delivery. **b**, Visual summary of plasticity in synapses and memristors. The proposed SVDP with unipolar plasticity allows selective depression or potentiation by programing different positive-voltage spikes with fixed frequency and different timing intervals. This process fundamentally differs from spike-rate-dependent plasticity and spike-timing-dependent plasticity. **c**, Schematic of ionic migration among MTPP molecules. M = Zn, Ni, Co, Fe–Cl, and 2H lead to ZnTPP, NiTPP, CoTPP, FeTPPCL, and TPP, respectively. **d**, Configuration of ITO/MTPP/ AlO_x /Al. The drift of internal oxygen ions (O^{2-}) dictates the switching behavior.

Figure 2

Electrical characteristics of ZnTPP/AlOx device. a, Typical I–V curve showing a pinched hysteresis loop at positive and negative bias voltages. The voltage was swept from zero to 10 (–10) V, then back to zero. b, c, Hysteric I–V loops of the ZnTPP/AlOx devices during 10 voltage-sweep cycles of 0 $\rightarrow$ 10/–10 V $\rightarrow$ 0 and 0 $\rightarrow$ 4/–4 V $\rightarrow$ 0, respectively. The device conductivity continuously increases (decreases) during the positive (negative) voltage sweeps. d, e, Conductance versus sweep cycles in potentiation and depression, respectively. f, Voltage-dependent conductive variations.

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STEM-EDX characterization and mechanism of the ZnTPP/ AlO_x devices. a, STEM images and corresponding STEM-EDX elemental mapping of O (blue) in the virgin (i and iii) and energized (ii and iv) samples under a voltage bias of +7 V. b, Elemental line-scanning profiles from the Al to ITO sides [marked by white lines in a (i and ii)]. c, Typical high-resolution O 1s and Zn 2p XPS spectra. Data were collected from the pristine state after electrode polarization. d, Schematic of the proposed model. ZnTPP regulates memristive behavior by functioning as an ionic/electronic media. e, Schematic of O^{2-} redistribution under a weak (upper panel) and intense (bottom panel) external electric field.

Figure 4

Proof-of-principle design of SVDP-based filtering with unipolar plasticity. a, Working process of visual recognition systems in the human brain. Photonic signals are converted into electric signals, and background or noise is efficiently filtered by the neuron–synapse network. b, Visualizations of the memorizing processes in an ideal case. c, Noise filtering with and without the SVDP mode. Each pixel represents a single memristor.

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