RESEARCH OF NON-VOLATILE MEMORY AND NEUROMORPHIC COMPUTING BASED ON 2D FERROELECTRIC PEROVSKITE

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Research of Non-volatile Memory and Neuromorphic Computing based on 2D Ferroelectric Perovskite

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A thesis submitted in partial fulfillment

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Certificate of Originality

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Abstract

With the advancement of artificial intelligence and machine learning, electronic devices have become a burgeoning research field and a cornerstone of modern Internet science progress. Prior to the advent of computers, manual calculations were the sole reliance for task completion, albeit with no guarantee of accuracy. In the 1950s, von Neumann, recognized as the "father of modern computers," delineated the fundamental components of computers, encompassing input devices, output devices, controllers, arithmetic units, and memory. Among these, the arithmetic unit and controller collectively form the Central Processing Unit (CPU). Nonetheless, despite decades of evolution, substantial breakthroughs in computer performance based on the von Neumann architecture have proven elusive. Confronted with the technological landscape of today's intelligent era, scientists are increasingly focused on enhancing energy efficiency. Consequently, a paradigm shift in architecture is imperative to surmount the existing bottleneck, addressing issues such as the performance cost associated with frequent data transmission between memory and arithmetic units, sluggish transmission speeds, and other performance-related challenges.

Diverging from the conventional von Neumann architecture, artificial intelligence chips typically engage in the collection, transmission, processing, and storage of information by emulating the neural network of the human brain for information perception and decision-making. This approach is better suited for integrating

information distributed computing and storage on hardware platforms, particularly in scenarios involving multi-sensory cross-modal data and intelligent task processing applications (e.g., image and speech recognition). The pronounced advantages of artificial intelligence chips in power consumption, energy efficiency, and hardware overhead are substantial, motivating numerous scholars to further the development of such devices.

The material synthesis part of this thesis focuses on the utilization of two-dimensional perovskite. Perovskite, being a novel type of optoelectronic material, possesses the advantageous characteristics of two-dimensional materials like solution processing and easy preparation, while also retaining the inherent traits of perovskite materials such as light responsiveness and low energy loss. Consequently, it has emerged as a prominent subject within the realm of material research, garnering considerable attention.

In this study, Dion-Jacobson (DJ) phase 2D perovskites have been selected as the active layer material, employing the spin-coating method to facilitate the fabrication of large-area devices. The device fabrication process involves the use of a metal-perovskite-metal sandwich structure.

Regarding applications, the focus lies on the advancement of new neuromorphic device technology, involving the creation of intelligent chips founded on the neuromorphic transformation of traditional CMOS, as well as the development of neuromorphic chips reliant on novel devices. Moreover, this thesis delves into the future developmental trajectory and highlights areas necessitating enhancement within the experimental process.

Acknowledgments

During two years study at PolyU, this was an unforgettable and colorful experience here. I have learned a lot of knowledge, scientific research process, etc., and all the growth will become the cornerstone of future efforts.

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My supervisor exhibits meticulous attention to detail in every experiment we undertake. Whenever I encountered obstacles within the project, he engaged in through discussions with me and provided invaluable guidance. Additionally, during my time in Hong Kong, he demonstrated genuine concern for my well-being, addressing my health concerns and advocating for a balanced lifestyle. Professor Loh transcends beyond being solely an academic mentor; he embodies the role of a life mentor, and I am profoundly thankful for his support and care throughout my academic tenure of two years.

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In life, we always meet close friends in many unexpected moments. I will remember every experience. I hope I can move forward with more strength in the future.

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Chapter I

Introduction and Literature Review

1.1 Introduction and Background

With the development of artificial intelligence and machine learning, electronic devices are an emerging hot research field and the foundation of modern Internet science progress. Neuromorphic computing is a form of computing that enables simultaneous processing and storage of information[1], potentially overcoming the constraints of the von Neumann computing architecture caused by limited data transmission speed between the central processing unit (CPU) and memristor (memory). The purpose of scientists' research on artificial synaptic electronic devices is to simulate the signal storage and processing functions of biological synapses, and it is considered to be the basis for making artificial neural networks and neuromorphic computers. Synaptic plasticity is the basis of the brain's signal processing, memory and learning.

Currently, the artificial intelligence has become ubiquitous in our daily lives and work, the shortcomings of traditional von Neumann architecture device, like the limitation of scalability and high energy consumption, are becoming increasingly apparent.[2]

Fortunately, lots of recent research works have proven that the analog in-memory computing has potential to overcome these challenges,[1] but how to achieve it still needs to be solved urgently.

The development of artificial neurons plays a crucial role in bridging the connection between humans and machines in various applications.[3] Scientists now are trying to convert weak stimuli, such as electrical stimulation (voltage stimulates), into pulse signals resembling the human sensory system. For example, electrical stimulation serving as artificial neurons holds promise for advancing medical neuroprosthesis technologies, neural prosthetics, sensor technology, and other frontier fields of science and medicine.[4] Furthermore, in the field of neural computing, with the prerequisite of mature technology, it is also feasible to achieve large-scale sensor-integrated computing.

Post-CMOS, there is a strong drive to understand and control some properties interplay in the materials or devices, such as, spin direction, ferroelectricity, and electromigration properties, etc.[5] Multiferroics (MF) enables electrical writing of memory bits and non-destructive magnetic reading of multistate memory devices. Ferroelectrics are a type of polar dielectric material with spontaneous polarization, whose spontaneous polarization vector can be reversed with an external electric field. They have unique electrical, optical, mechanical, acoustic and thermal properties as well as the function of mutual coupling or conversion between them.[6] The integration of ferroelectric thin films and semiconductors has produced a new generation of memory. It has low power consumption, fast writing speed, many rewrite times and strong radiation resistance, which plays a great role in the field of semiconductor memory.

Three categories of memories that used ferroelectric property layers have been documented based on distinct materials: inorganic, organic polymer, and 2D material devices.[5] The Inorganic memory devices were initially reported with superior ferroelectric properties of inorganic materials, such as $BaTiO_3$, $PbZrTiO_3$, and $BiFeO_3$. However, these devices usually require specific conditions or strict matching of materials. Therefore, in recent years, devices made of 2D materials have been widely studied and rapidly developed, such as In 2D materials,[8] perovskite semi-conductor layer, etc. Most of these methods use vapor deposition and exfoliation to prepare single-layer/few-layer two-dimensional materials, and it is still difficult to achieve large-area ferroelectric two-dimensional material devices. In this thesis, I will use spin-coat method to make large area 2D perovskite layer as the active layer. I chose to use DJ organic-inorganic hybrid perovskite as the interlayer material, which has become one of the most promising materials due to its advantages such as low-cost materials and easy solution processing. The emergence of memristors provides new opportunities for achieving high-performance neuromorphic computing.

1.2 Literature Review

At present, the structure of devices is mainly centered around three-terminal structures and two-terminal structures. The two-terminal structure is relatively new in current research because it is simple in structure and has more development and research prospects. It can record the change of its resistance according to the applied voltage and current, and is often used in the fields of resistive switches and artificial synapses.

Comparing with three terminal devices (Figure 1), the structure of the two-terminal halide perovskite devices is metal–perovskite–metal, which shows the important promising for neuromorphic computing due to their low power consumption, easy to be fabricated, and rapid response.[4,6,7]

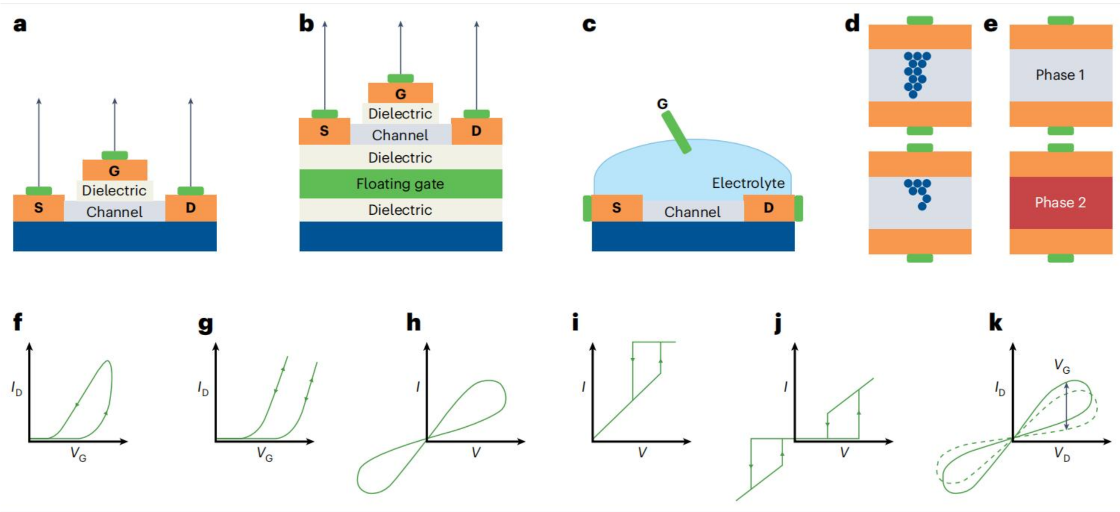


Figure 1 Three terminal and its different kinds of IV curves

With the research development based on two-terminal resistive switchable halide perovskite devices, their operation relies on the migration of halide ions or other ions toward the electrode and the movement of halide vacancies toward the cathode,[22] some of which create conductive filaments. Additionally, the low-resistance paths created by filaments can be broken when applied a opposite polarity voltage. Tae-Woo Lee's group[23] first reported about two terminal perovskite synaptic device based on $MAPbBr_3$ perovskite. The device exhibits synaptic functions, including short-term plasticity and long-term plasticity, arising from the migration of bromide anions, which resulted by the external electrical pulses. After applying multiple pulses, numerous ions migrated over long distances, and plenty of ions were trapped at the metal/perovskite interface,[4] resulting in some halide sites in the perovskite film to become empty, thus forming a conductive path.

Two-dimensional materials with ferroelectricity and non-volatile memories continue to captivate the interest of researchers in the fields of materials science, condensed matter physics, and nanodevices.[12] Devices with ferroelectric properties active layer play a vital role in realizing non-volatile memories which is also an promising phenomenon in the 2D area.[9] In a two-terminal structure composed of a ferroelectric thin film layer and two electrodes, more attention attention should be paid to the interface barrier height between the ferroelectric material and the electrode caused by polarization. In order to obtain better switching performance, Majumdar and his group made a two-terminal ferroelectric memristor with the following structure Au / P(VDF-TrFE) / ITO, in which the thin film was made by the spin coating approach.[11] Due to the thin copolymer tunnel barrier, a significant resistive switching effect can be obtained, with long holding behavior and good switching stability.

Prof. Shi's group demonstrated the two-terminal ferroelectric synapse based on the van der Waals halide perovskite material (R-CYHEAPbI_3), the synapse device structure is Au / R-CYHEAPbI_3 / n-Si, the vdW halide perovskite has precisely the advantages of material dimensionality, excellent optoelectronic properties, and material processing conditions that provide more opportunities for designing this device. It exhibits voltage-pulse-dependent weight modulation with a total on:off ratio of 50 and good endurance up to 107 cycles.[24] The devices also show good STP, LTP, and other spike-timing-dependent plasticity,etc.

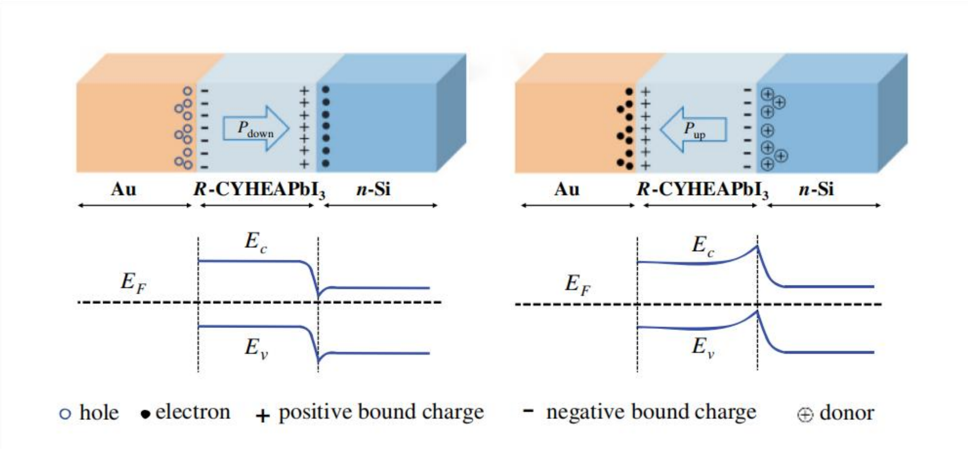


Figure 2 Ferroelectric polarization points to n-Si interface (Pdown) after applying positive Vw and the opposite direvtion shown from Shi's article

The photoelectric properties of perovskites have been mentioned in many synapse studies, such as using ITO as an electrode and using different light intensities and intervals to verify the outstanding characteristics of the device. Prof. Huang' s group reported that two-terminal organometallic tri-halide perovskite (OTP) synaptic devices can mimic neuromorphic learning and memory processes.[25] Various functions known from biological synapses were demonstrated, including four forms of STDP, SRDP, STP, and LTP as well as learning-experience behaviors. The photovoltaic device also supports optical readout of synaptic functions. Perovskite synapses have the potential for low energy consumption, close to that of biological synapses.

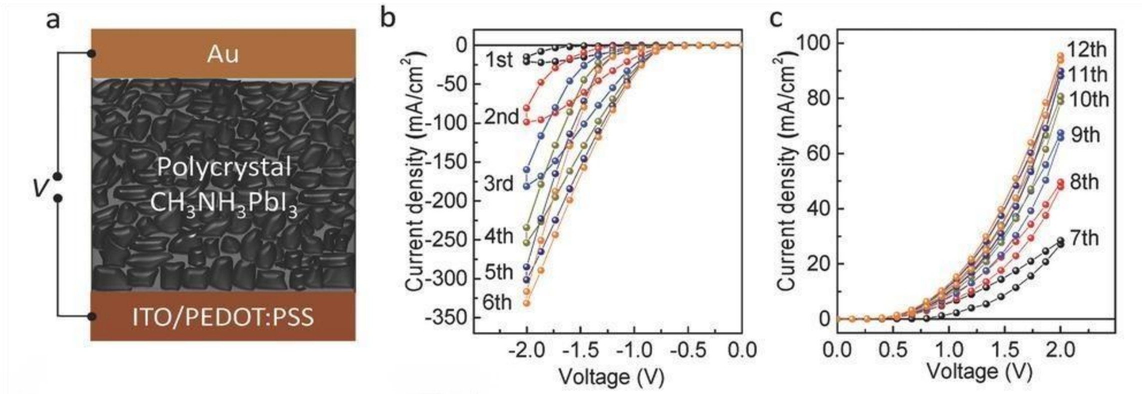


Figure 3 ITO / Polycrystal (CH3NH3PbI3) / Au device data from Prof Huang's group

There are also some studies based on all-inorganic perovskite memristor in neuromorphic computing. Prof Liu's group prepared a memristor device with Au / $CsPbBr_3$ / ITO structure,[26] which exhibited resistance switching behavior. After 400 switching cycles, there was no obvious attenuation of high and low resistance states. The memristor device can simulate biological synaptic plasticity by stimulating it with voltage pulses. Moreover, they also built a training/recognition database with higher accuracy than other memristor-based neural networks. These phenomena all show that perovskite-based memristor devices have great potential in neuromorphic computing systems.

Besides, Prof. Luo's gourp used spin coating method to prepare $CsPbI_3$ thin films, and the artificial synapses of the prepared Au / $CsPbI_3$ / ITO structure showed learning and memory behaviors similar to biological neurons.[29] This method of simulating the properties of neural synapses is relatively simple and low-cost.

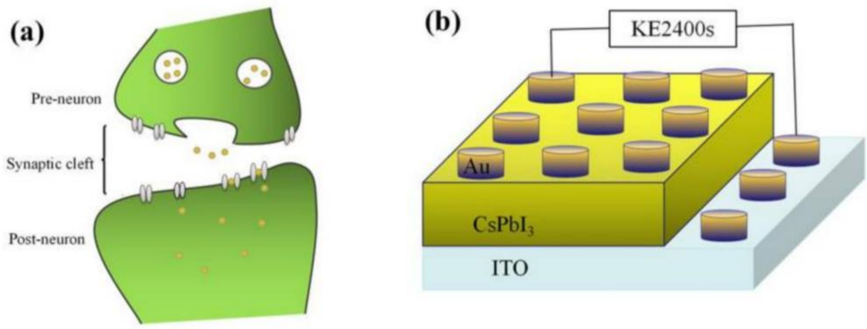


Figure 4 (a) A pair of synapses in biology;

(b) the structure of the artificial synapse is Au/CsPbI3/ITO.

Notably, ferroelectric halide perovskite has been reported recently that it has good voltage-pulse-dependent weight modulation performance in a two-terminal ferroelectric synapse.[10] This shows that the polymorphic regulation of perovskite conductivity is closely related to ferroelectricity, voltage, light and other reactions and is worthy of further research and development.

1.3 Research motivation

First, artificial synapses, as one of the important components of neuromorphic circuits, mimic the memory and learning methods of biological synapses in the human brain. It is important to try to prepare such devices for simulating and realizing another breakthrough in biosensing. In order to achieve efficient neuromorphic computing, the devices prepared by researchers must have properties such as linear and symmetric weight excitation relationships, a large number of non-volatile states, and rapid switching speeds. Next, in the extensive publication of synaptic devices, research on ferroelectric multi-state memristor synapses has recently attracted attention. They exhibit large polarization, reasonable number of synaptic states, good durability, and good retention. However, the processability and defects of the materials have always been problems for their stable operation.

Therefore, the halide perovskites with excellent electrical and optical properties have become a new research hotspot, which has great feasibility and provide opportunities to solve some of the problems suffered by ferroelectrics. In this thesis, I choose to use perovskite materials for research. The selection of Dion - Jacobson (DJ) phase perovskites is well-justified for their unique properties suitable for neuromorphic computing. DJ phase perovskites exhibit high structural stability, ensuring reliable long-term device operation. Their tunable interlayer spacing and chemical composition allow precise control of electrical and optical properties, making them suitable for neuromorphic computing. They possess excellent ferroelectric properties, crucial for mimicking biological synapses, and enable low-power operation, enhancing energy efficiency in large-scale devices. Interface engineering in metal-perovskite-metal structures optimizes electrode contact, improving device performance and reliability. Additionally, their versatility extends to both electrical and optoelectronic synaptic devices, supporting multimodal neuromorphic computing. DJ perovskites also offer good solution processability, facilitating large-area manufacturing and integration with existing semiconductor processes.

1.4 Significant of Research

As the computational demands of the Internet continue to grow, von Neumann architecture processing built using digital circuits has reached saturation in terms of computational power and power, necessitating the investigation of alternatives.[12] Memristors can simulate the functions of both storage and computing in the human brain, aiming to break through the von Neumann framework. Memristor-based brain-inspired systems are appealing for their exceptional parallelism, low energy consumption, and robust fault tolerance, making them a promising avenue for scientific exploration. The instability in the formation and dissolution of conductive filaments within conventional memristors restricts their ability to the functionality of biological synapses. Consequently, there is a burgeoning interest in the utilization of simulated neural synapses as a focal point of research.

Ferroelectric memristors can overcome the shortcomings of traditional memristors because their resistance change depends on the polarization flip of the ferroelectric film. The two-terminal device is different from the traditional FeFET, which can achieve stable storage characteristics and has the potential for multi-level storage. By regulating the polarization response of ferroelectrics, the resistance of the memristor can be adjusted by the flipping of ferroelectric domains. Furthermore, if multiple resistance states with bidirectional continuous reversibility can be obtained, this is similar to the change of synaptic weights, such as, STP, LTP,SDTP, etc. Most publications have simulated primitive neural morphologies[13], anticipating that memristors with higher-order complexity could solve problems that would otherwise require complex circuits.

The two-terminal device is different from the traditional FeFET, which can achieve stable storage characteristics and has the potential for multi-level storage. Based on current research, I fabricated a DJ perovskite and used this out-of-plane perovskite as the active layer of a two-terminal Au/Perovskite/Au device to study synaptic performance under different voltage conditions.

Chapter II

Introduction and Literature Review

2.1 Experimental Methodology

In this chaper, the main Dion-Jacobson perovskite (DJP) materials used are: (AMP)(MA)Pb_2I_7, (AMP)PbI_4, (AMP: 4-(aminomethyl)piperidinium compound (Abbreviated as $DJP_{n=1}$ and $DJP_{n=2}$)[14-15]). In this experiment, the solution method and crystal supersaturation precipitation method were used to prepare the 2D perovskite materials. The perovskite precursor solution was prepared according to the proportional concentration, and the perovskite layer was spin-coated on the substrate by spin coating. The fabrication of the device used a sandwich structure (metal-perovskite-metal) and the inert electrodes were made by evaporation.

2.2 Dion−Jacobson Hybrid Perovskite of (AMP)(MA)Pb_2I_7 ($DJP_{n=2}$)

(a) Prepare $AMPI_2$ and MAI

4-(aminomethyl)piperidine (AMP) was used directly to prepare $AMPI_2$ in hydroiodic acid (HI). AMP was purchased from Sigma Aldrich and used as received. Methylammonium (MA) were purchased from Sigma Aldrich and used as received.

AMP was used directly to prepare MAI by 57% hydroiodic acid (HI). Solution should be kept in low temperature (around 4°C).

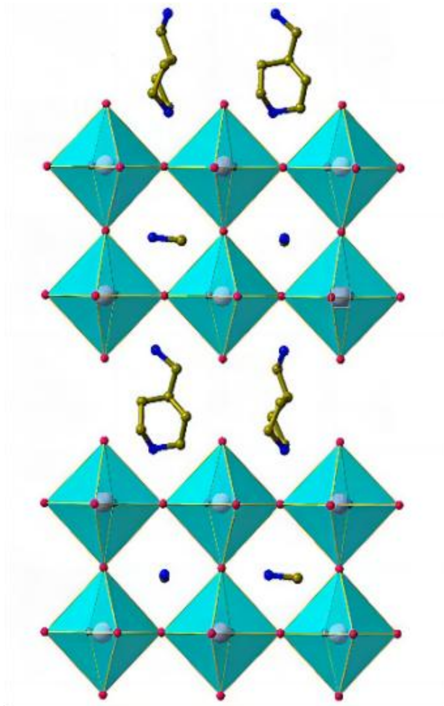


Figure 5 Crystal structure of $DJP_{n=2}$

(b) Synthesis of [(AMP)(MA)Pb_2I_7]

lead(II) iodide 4-(aminomethyl)piperidinine/methylamine DJ phase perovskite, n = 2 ($DJP_{n=2}$). A mixture of $AMPI_2$, MAI (or MA) and PbO dissolved in concentrated HI solution was placed in a 20-mL glass vial, followed by the addition of H_3PO_2. The vial was sealed and kept at 110 ℃ with stirring for 1 hour. Subsequently, the vial was cooled to room temperature over 10 hours. Dark-red colored single crystals of $DJP_{n=2}$ were obtained. The concentration of the perovskite precursor solution prepared by crystals is about 0.4 M.

2.3 DJ Phase Hybrid Perovskite of (AMP)PbI_4 ($DJP_{n=1}$)

(a) Solution Method

Combine $AMPI_2$ powders, MAI powders in the solution of hydroiodic acid (HI), according to different concentration ratios, the final suitable range is about 0.4M ~ 0.6M. Powdered reactants were all purchased from Aladdin company.

(b) Crystal Synthesis Method

The same method as DJPn=2 crystal synthesis process. Using AMP, MA liquid reagents (purchased from Sigma Aldrich and used as received), the proportional concentration is lower than that prepared with DJPn=2. After the solution is prepared (H3PO2 should be added), and heat at 110 °C with stirring for 1 hour. The concentration of the perovskite precursor solution prepared by crystals is about 0.4 M.

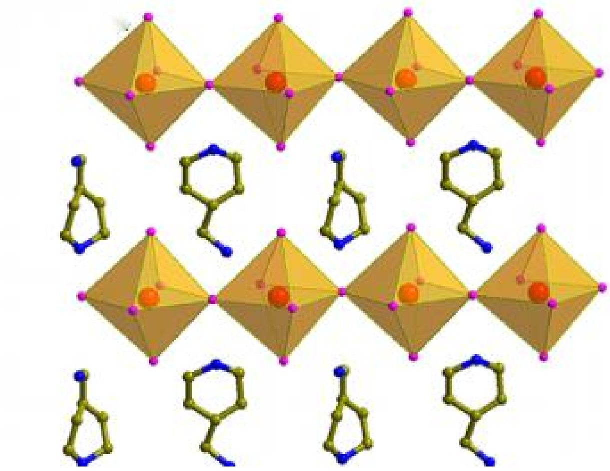


Figure 6 Crystal structure of $DJP_{n=1}$

2.4 Experimental Section

Raw materials

All chemicals were purchased from commercial vendors (reagent grade) and used as received.

Experimental equipment

(a) Spin coater

(b) Glove box with nitrogen atmosphere

(c) E-beam evaporation system

(d) Electronic tests were recorded by LakeShore Probestation (Model CRX-6.5K) equipped with Keithley 4200 Semiconductor Characterization System

Characterization

(a) Powder X-ray diffraction (XRD)

X-ray Diffraction (XRD) stands as a predominant method employed for investigating the physical phase and internal structure of target samples. Whether examining crystalline or amorphous samples, when subjected to X-ray irradiation, they exhibit distinct diffraction phenomena. The alterations in diffraction patterns are closely linked to factors within the material, such as composition, crystal structure, intramolecular bonding, molecular configuration, and conformation, all of which play a pivotal role in shaping these patterns.

In delving deeper into the analysis of diffraction patterns, key characteristics encompass the spatial distribution and intensity of the diffraction lines. The spatial distribution is influenced by various factors within the unit cell, encompassing size, shape, and orientation. Moreover, the type and positions of atoms within the unit cell account for disparities in intensity levels across the diffraction patterns.

(b) Photoluminescence (PL) characterization

PL is the phenomenon where an object absorbs energy from an external light source, becomes excited, and subsequently emits light. This process typically involves three main stages, as illustrated in Figure 7: (1) absorption, (2) energy transfer, and (3) light emission. Both the absorption and emission of light involve transitions between energy levels, passing through excited states. The energy transfer stage is characterized by the movement of these excited states.

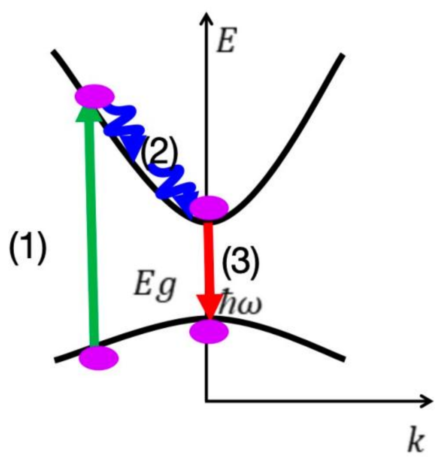


Figure 7 The schematic diagram of PL, which generally goes through three main stages: (1) absorption, (2) energy transfer and (3) light emission.

Besides, PL characterization can be categorized into direct bandgap PL and indirect bandgap PL, as illustrated in Figure 8. Direct Bandgap PL (Figure 8a): In a typical direct bandgap PL experiment, when the energy of the incident laser photon exceeds the bandgap energy of the material, the semiconductor enters an excited state. The incident photon is absorbed, creating electrons and holes at the top of the conduction band and the bottom of the valence band, respectively. These excited electrons and holes are unstable and, after a very brief period, the electrons relax their energy and momentum to the minimum value of the conduction band (i.e., the eigenstate). Eventually, the electrons recombine with the holes, releasing photons in the process.

Indirect Bandgap PL (Figure 8b): For typical indirect bandgap semiconductor materials, the excited electrons and holes occupy different momentum spaces. During the relaxation process, as the electrons transition to the ground state, the momentum mismatch requires interaction with phonons in the lattice. This interaction facilitates further transitions. Ultimately, through a series of transitions, the electrons return to the ground state and recombine with the holes, emitting light. During this process, a significant amount of photon energy (Ep) is consumed and converted into other forms of energy, primarily heat.

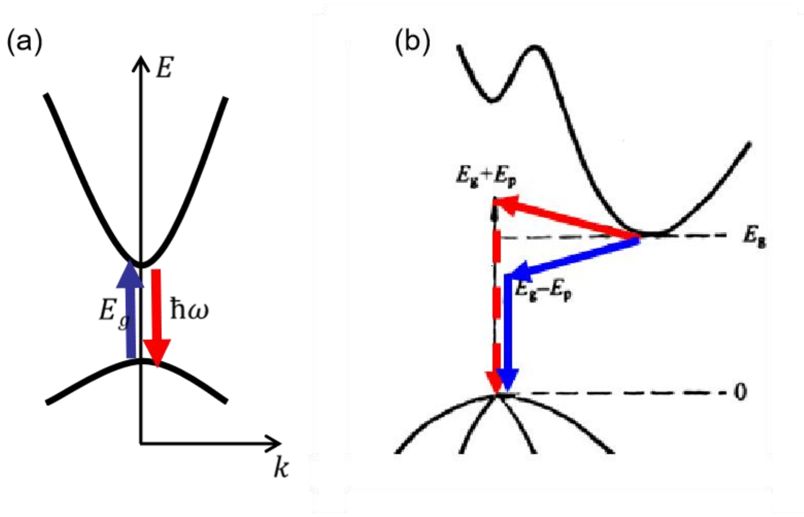


Figure 8 The schematic diagram of typical (a) direct bandgap PL and (b) indirect bandgap PL

In this work, we compared the PL spectra of two 2D perovskites with n=1 and n=2 to investigate the relationship between the number of layers (n) and their optical properties, such as electron-phonon coupling. The PL experiments were conducted using a WITec Confocal Raman microscope.

(c) UV-visible absorption spectroscopy

UV is a technique used to analyze and measure the absorption of radiation in the UV-visible light region by molecules of certain substances. This molecular absorption spectrum is generated by transitions between the electronic energy levels of valence electrons and electrons in molecular orbitals.

The basic principle of UV-visible absorption spectroscopy involves the electron transitions within the sample when it is irradiated with light. Special structures can exhibit unique electronic transitions, corresponding to different energies (wavelengths). These transitions are reflected as absorption peaks at specific positions and intensities in the UV-visible absorption spectrum. By analyzing the position and intensity of these absorption peaks, one can infer structural information about the sample being tested.

In this study, we compared the UV-visible (UV-vis) spectra of two 2D perovskites with n=1 and n=2 to further investigate the relationship between the number of layers and their optical properties, specifically focusing on the absorption peak wavelength. The UV-vis experiments were conducted using a Perkin Elmer UV-Vis-NIR Spectrometer.

(d) Piezoelectric force microscopy (PFM)

PFM is extensively utilized in the investigation of ferroelectrics and is of particular interest for the imaging of ferroelectricdomains at high spatial resolution. PFM functions on the basis of the inverse piezoelectric effect, wherein a localized electric field is administered to the sample surface, and the ensuing surface displacements are scrutinized. Methodologically, PFM is carried out concurrently with an Atomic Force Microscopy (AFM) scan of a ferroelectric surface utilizing contact constant force mode. An electrical bias is imposed on a conductive probe, thereby engendering a localized electric field underneath the probe. Owing to the domain structure typically inherent in ferroelectrics, applying the same local electric field to distinct surface areas leads to disparate outcomes.

In this study, PFM was employed to scrutinize and ascertain whether the synthesized perovskite material showcases ferroelectric properties, as well as to evaluate the quality of these ferroelectric characteristics.

Chapter III

Results and Discussion

3.1 Characterization of DJ perovskite

Following the synthesis of perovskite materials, the characterization of perovskite crystals was conducted. The X-Ray Diffraction result, as shown in Figure 9 and Figure 10, reveal that the crystal with DJPn=2 exhibits a close resemblance to the simulated XRD data, with a substantial overlap of peaks. From the data shown below (Figure 11) were Photoluminescence of $DJP_{n=1}$ and $DJP_{n=2}$, it can be seen that their absorption peaks and emission peaks are not consistent.

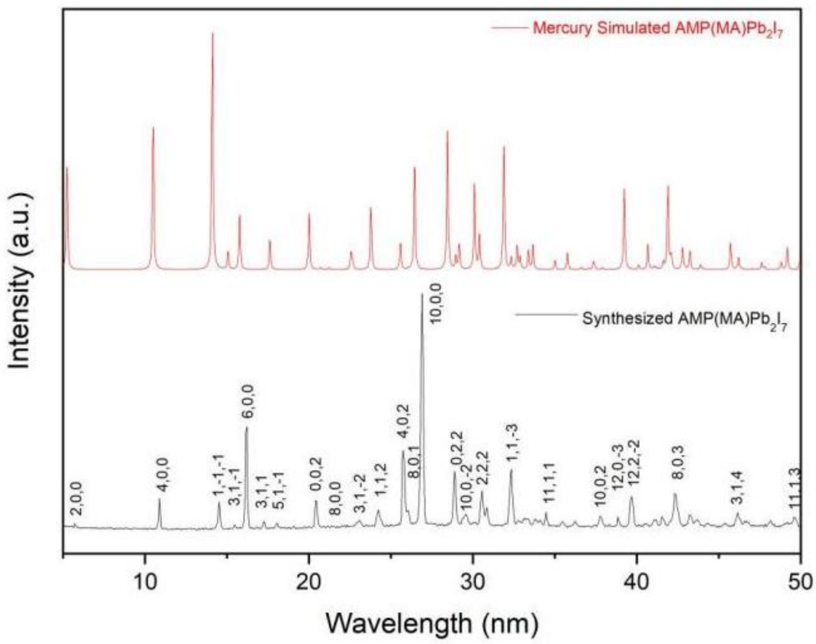


Figure 9 XRD of $DJP_{n=2}$

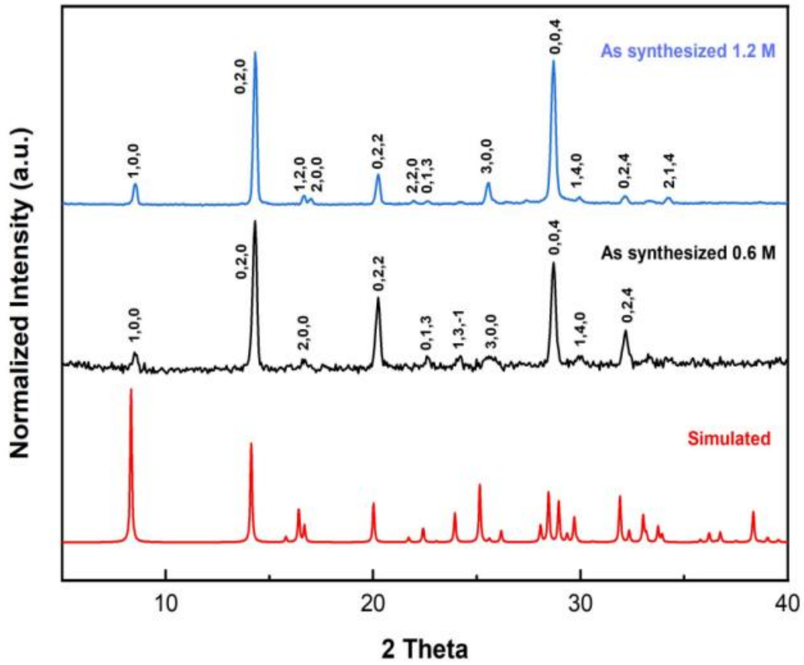


Figure 10 XRD of $DJP_{n=2}$

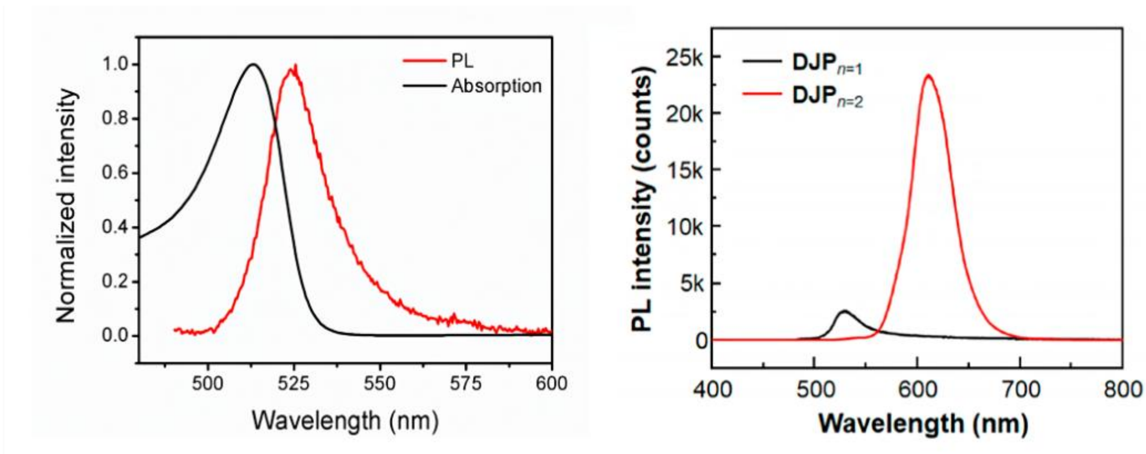


Figure 11 Photoluminescence of $DJP_{n=1}$ and $DJP_{n=2}$

Two-dimensional perovskite nanoplates with varying n-values exhibit distinct optical bandgaps and differing energy levels for the conduction band minimum (CB) and valence band maximum (VB).[32] When n=1, the material is a single layer; when n increases, the number of layers increases and the properties of the material change accordingly. Different n values affect the optical and electronic properties of perovskites, such as band gap, carrier mobility and stability.

The polarization switching can be checked by collecting I−V curve by semiconductor analyzer (Keithley 4200). The device was fabricated using a 200 nm ~ 300 nm thickness DJP thin film with Au / Ag electrodes (Figure 12-13). Obvious current peaks at ±7.6 V, corresponding to the coercive voltage, indicating the resistance changes due to the polarization switching of the DJP. The green arrow shown in the figure shows the voltage sweep direction.

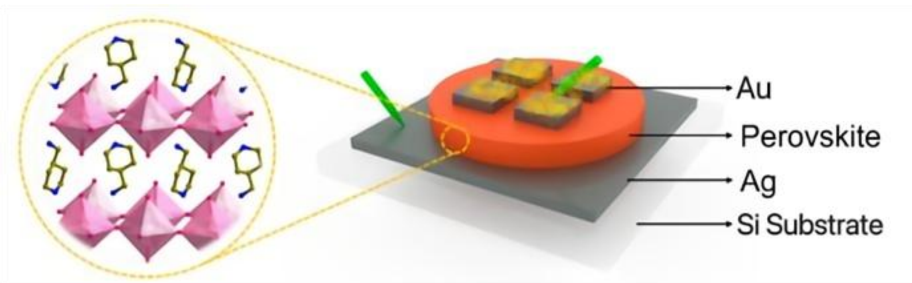


Figure 12 Au/Perovskite/Ag device structure

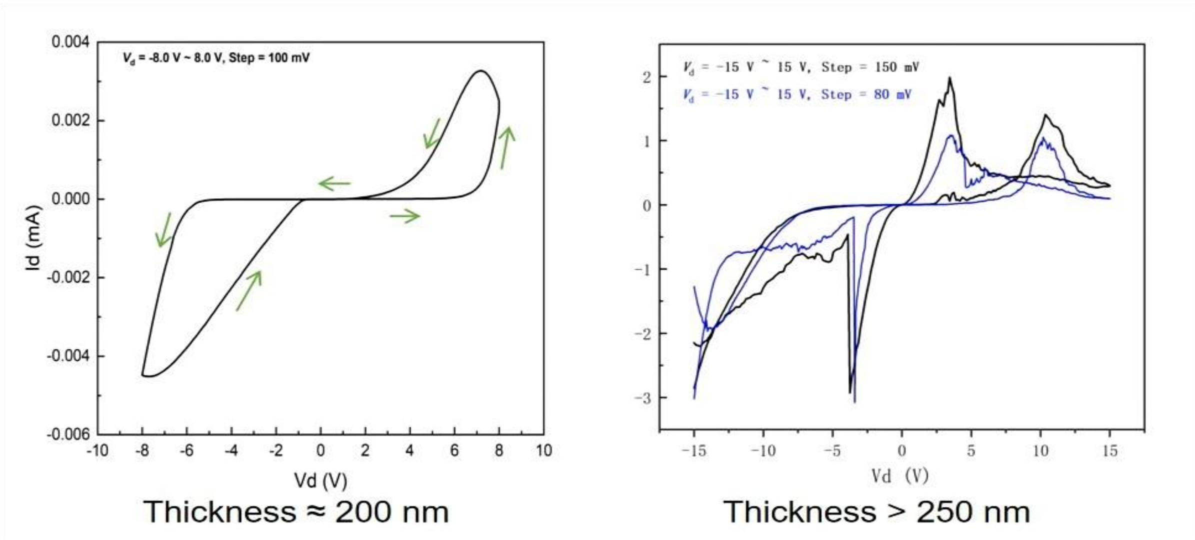
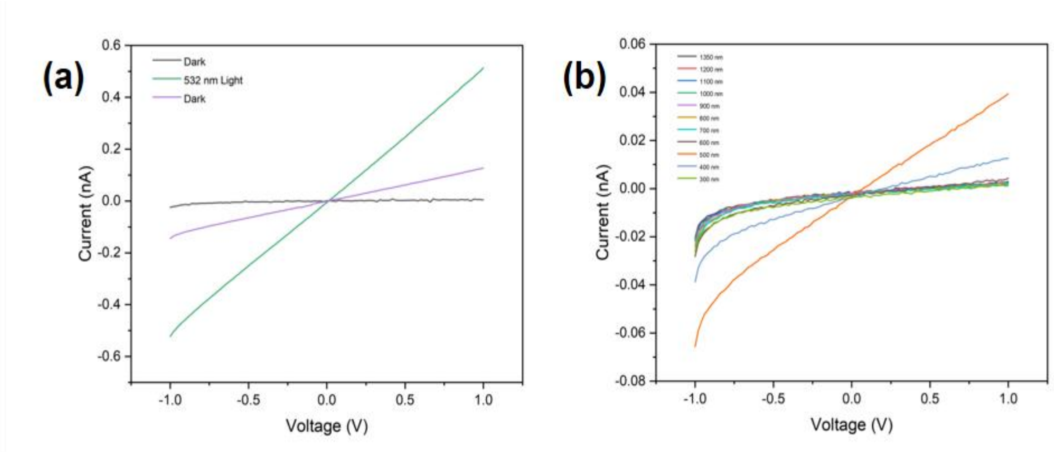


Figure 13 Au/Perovskite/Ag device I-V test results

In reality, beyond electrical stimulation, exposure to light can also activate neurons. External illumination serves as an effective regulatory mechanism; fluctuations in light intensity can adeptly modulate neuronal activity, thereby impacting the organism. To evaluate the photoresponse property of perovskite, light of varying wavelengths (ranging from 300 nm to 1300 nm) is intermittently administered to assess the sensitivity of the perovskite material. Evidently, the perovskite exhibits a robust light response within the green light spectrum (approximately 530 nm) as illustrated in Figure 14. Furthermore, when the light intensity within this range cyclically fluctuates at fixed intervals, the current demonstrates a gradual decline in accordance with the light stimulus intensity.



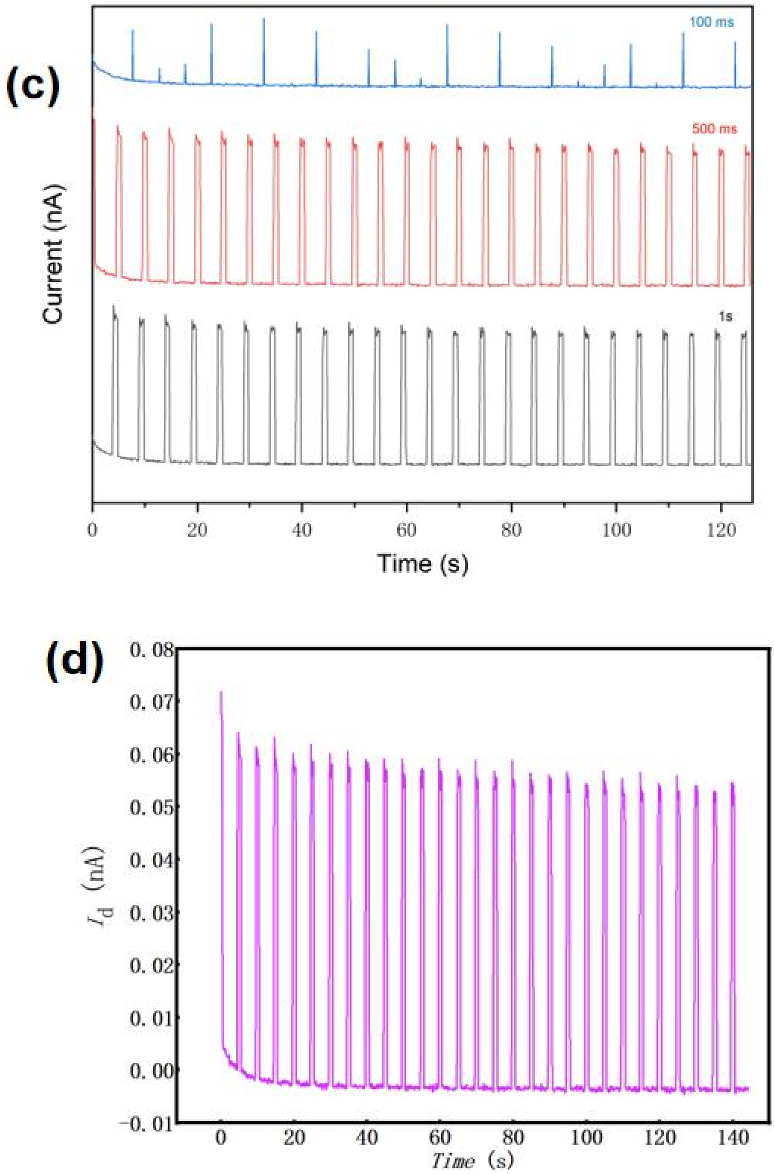


Figure 14 (a-b) DJPn=2 photoresponse under dark/532nm light/dark and in different light;

(c) Light pulse I-t characteristics by voltage 1V; (d) I-t curve (500 ms pulse)

3.2 Fabrication of Two-terminal device

A two-terminal structure of a 2D Dion-Jacobson perovskite memristor was constructed with the configuration Au(40nm) / Perovskite / Au(50nm), where the perovskite material employed was $(AMP)PbI_4$, featuring a perovskite layer thickness of 125 nm.

Upon fabricating the device with interdigitated electrodes measuring 100 um in width, the current flow significantly decreases when voltage is applied across it, as depicted in Figure 15. Applying an approximate voltage of 0.5V leads to the observation of an I-V hysteresis curve in the device.

Employing a circular copper mesh as a shading mask with electrode dimensions of 500 um results in a notable increase in current. An IV hysteresis loop is discernible at around 2V (Scan direction: -2V → 0V → 2V → 0V → -2V). In terms of non-volatile electrical testing, 3V pulses were introduced at intervals of 8s, 18s, 28s, and 38s, respectively (Figure 16). These pulses induced sudden changes in the current, causing alterations in resistance values that remained unchanged thereafter.

Regarding the process of device fabrication, it is advocated that the crossbar array structure (as shown in the figure below) can be used to cross-use horizontal and vertical electrodes to increase the possibility of integration. The simple geometry of the crossbar structure makes it easy to scale to higher densities, which is an advantage for the manufacture of large-scale integrated circuits. However, it should be noted that this structure sometimes causes leakage current. Due to the dense arrangement of the crossbar structure, the current may generate crosstalk between adjacent crossbars, which may cause signal interference and malfunction.

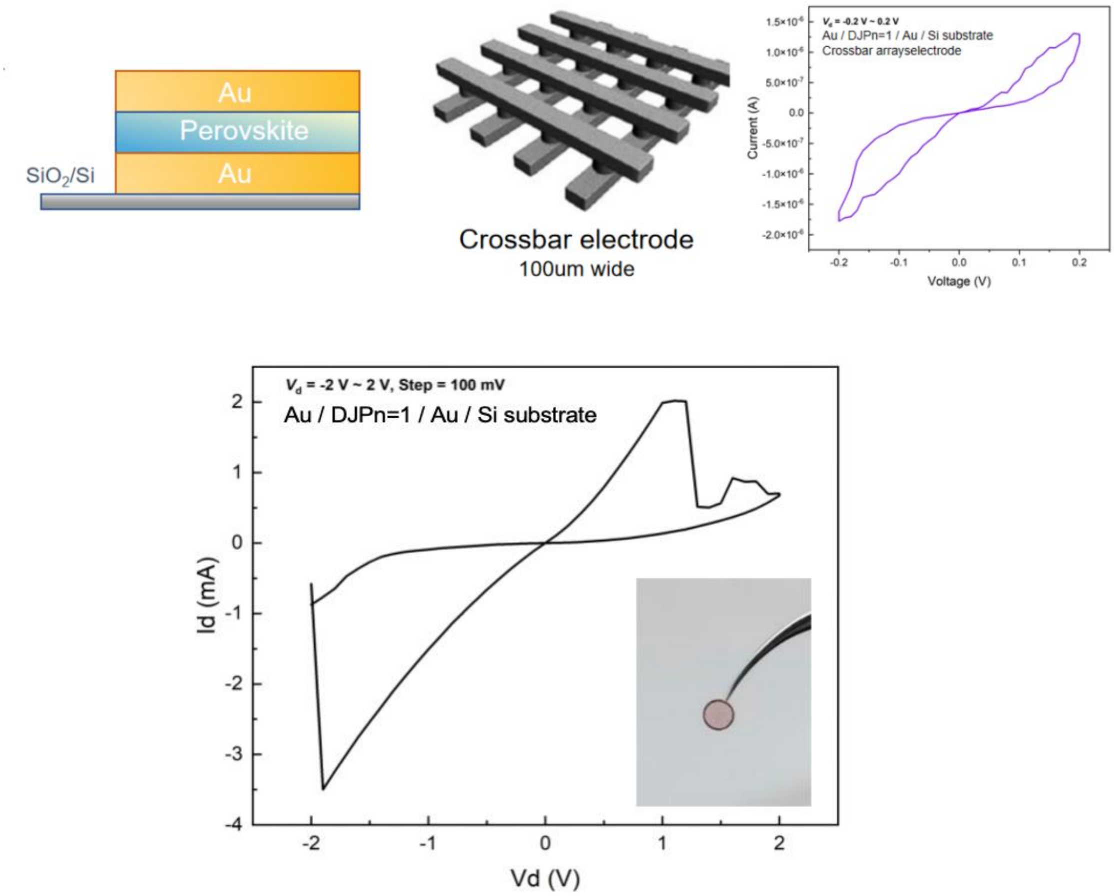


Figure 15 Device fabrication structure and I-V curve

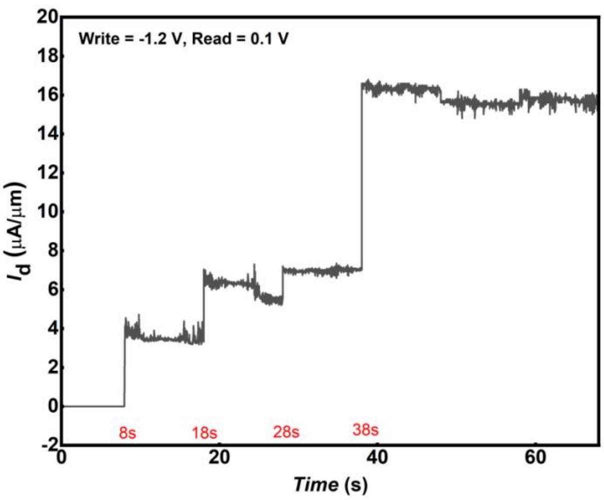
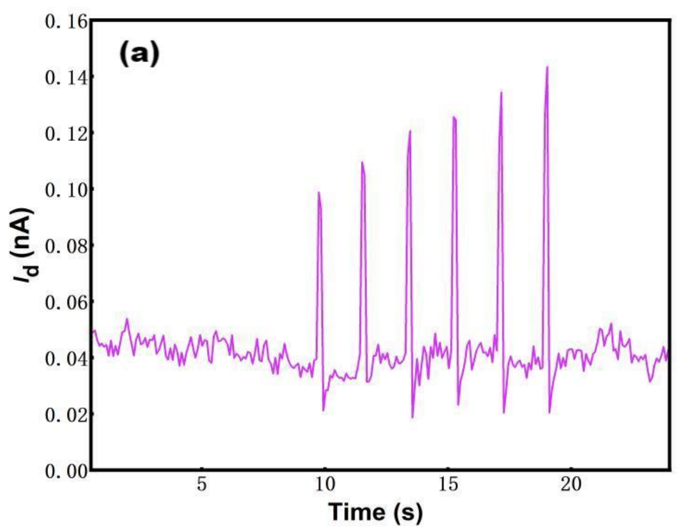


Figure 16 Device I-V curve of synaptic experiment

Since halide perovskite is a typical mixed ion-electron conductor, researchers have found a lot of evidence supporting the view of ion movement in halide perovskites through many spectroscopic studies, parameter evaluation, device modeling and simulation.[13-17] Different types of ions in the structure can move in the perovskite under external driving forces such as voltage, light, and temperature.[18-19] The role of the ferroelectric film in the device is to allow electrons to pass through the ferroelectric layer. When judging electrical data, the ion migration and polarization reversal of the ferroelectric properties are taken into account, resulting in a change in the current when the voltage is applied to a certain point. It has been previously demonstrated that both anionic and cationic vacancies are simultaneously involved in the realization of synaptic function, and a vacancy-mediated ion drift-diffusion mechanism has been proposed, but this still cannot explain in detail the retention caused by cations from a microscopic perspective.



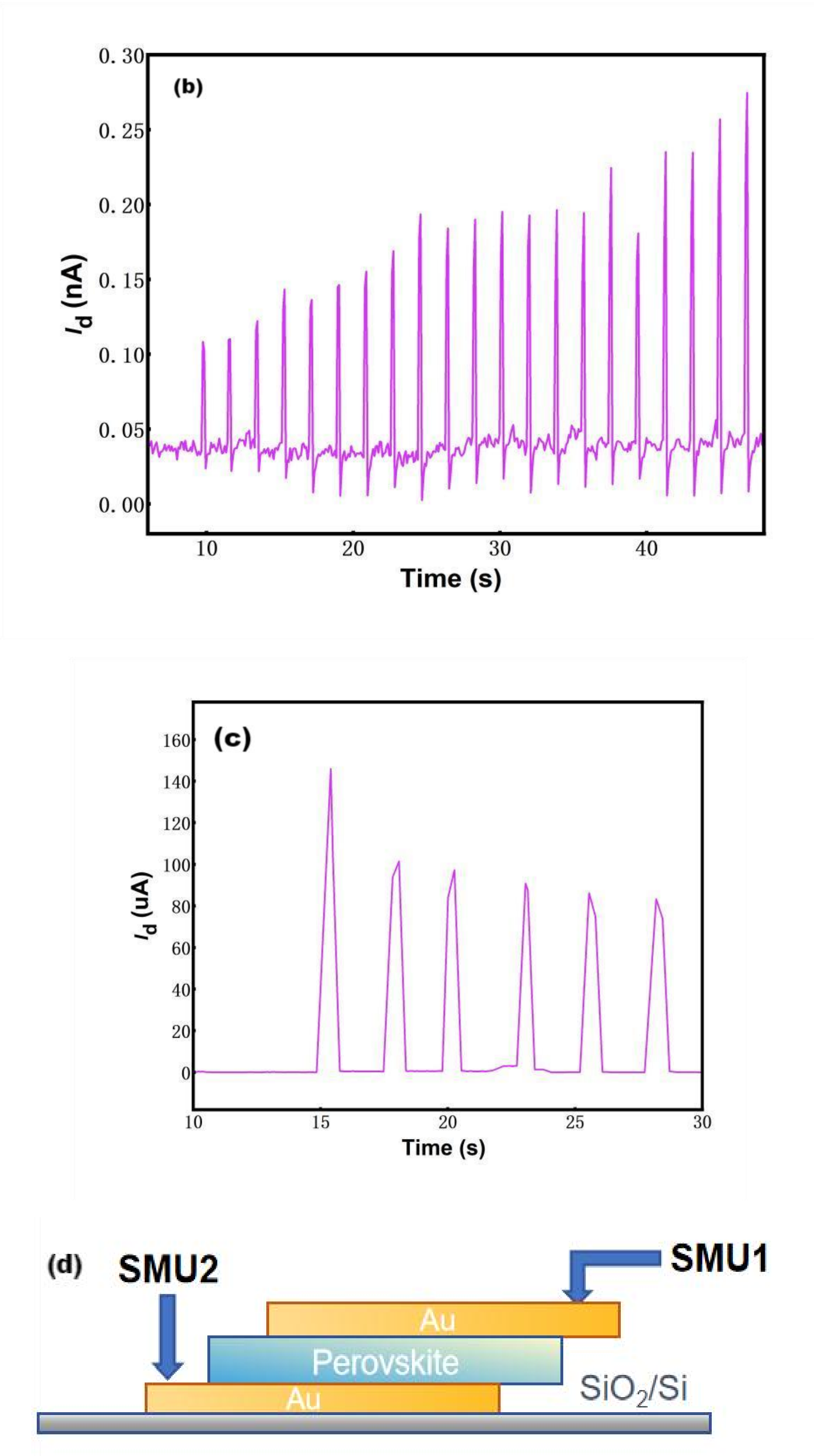


Figure 17 (a-b) Device I-t characteristics by voltage direction from top to bottom;

(c) Device I-t test by voltage direction from bottom to top; (d) Device structure

By measuring the I-V characteristic, using square wave pulses as input signals (voltage) to study the characteristics of the device is a key step in simulating synaptic function.[26] In this thesis, voltage pulses are applied to observe the changes in its IV curve.

The results are shown in the figure 17, it is noticeable that when programmed multiple voltage pulses on the device, the resistance value tends to decrease gradually under the stimulation of voltage pulse. However, when change the voltage direction (change the direction of the current flow), the trend tend to be opposite. Under repeated voltage stimulation, synaptic weights change from short-term to long-term states and show a tendency to potentiation or inhibition. The response of the excitatory postsynaptic current is regular.

When trying to change the top electrode with different work functions, the top electrode Au (5.1 eV) is replaced with TiN (~4.6 eV). TiN is one of the most commonly used materials for realizing electrodes and gates in CMOS devices. After replacing the top electrode with TiN, it was found that under continuous stimulation of 3V voltage, the current still showed this effect and reached saturation after several times (Figure 18). It can be clearly seen that this is a two-terminal volatile device. And the threshold switching voltages at both sides are different (+0.5 V and -1.8 V, respectively).

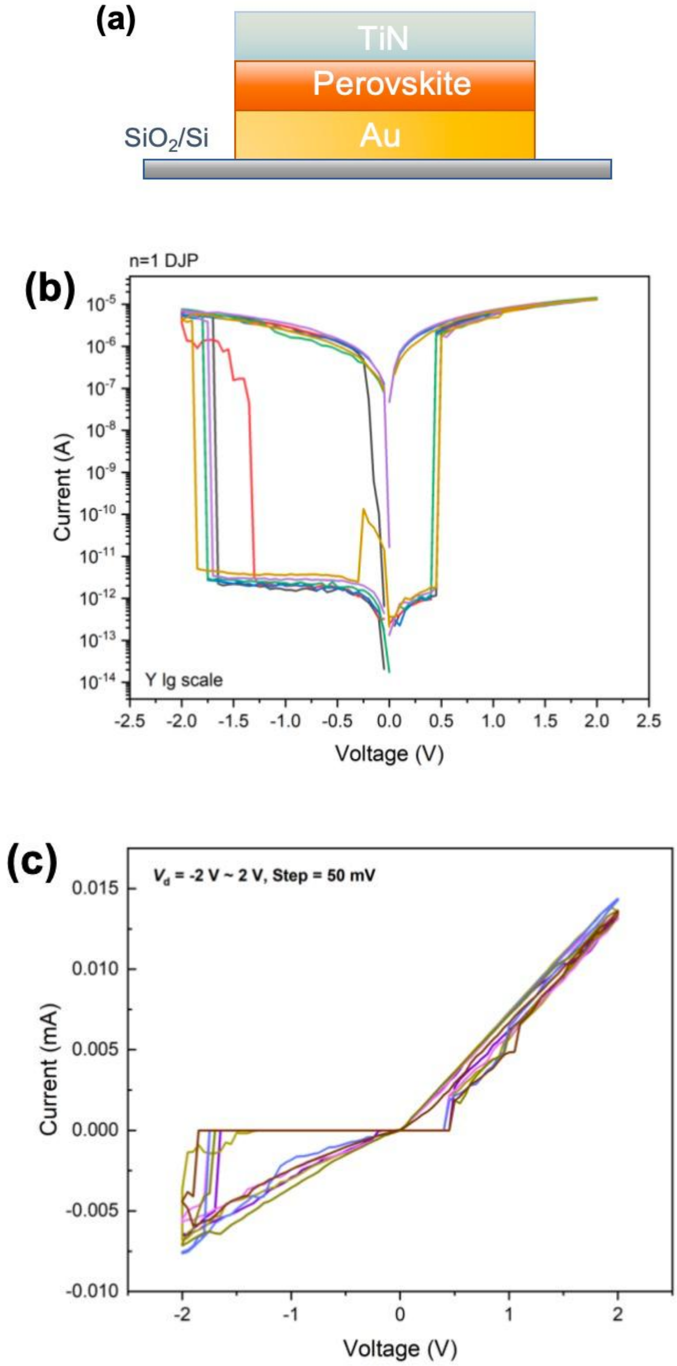


Figure 19 (a) Device structure; (b-c) device I – V characteristics

(scan by 0V ~ +2V ~ 0V ~ -2V ~ 0V) by different scale bar (lg scale and linear scale)

3.3 Application

Artificial intelligence stands as the primary driving force propelling a fresh wave of technological revolution and industrial transformation. As social progress calls for intelligent industrial advancements across various sectors, neuromorphic computing emerges with expansive application possibilities on the horizon. While strides and innovations have been achieved in brain-inspired neuromorphic computing, its advancement remains constrained by our current comprehension of its intricate neural network system and its practical application in biology.

Synaptic plasticity denotes the regulation of action potential strength through the augmentation or diminution of its efficacy, mirroring the biological processes underpinning facets like learning and memory. From an informatics perspective, brain-inspired research remains nascent, necessitating further advancement through enhanced interdisciplinary exchanges and collaborations across fields such as neuroscience, cognitive science, computer science, and microelectronics to foster comprehensive analysis and emulation. Notwithstanding the progress, numerous challenges persist.

Synapses play a pivotal role in transmitting signals between neurons and shaping the brain's memory and learning functions. The human visual system boasts exceptional real-time perceptual and visual data processing capabilities, pivotal in assimilating and sieving external information. In contrast to conventional machine vision systems hinged on von Neumann architecture, bionic neuromorphic vision systems seamlessly amalgamate sensing, memory, and processing functions. The fusion of 2D direct bandgap materials with ferroelectric materials in heterostructures showcases promise for neuromorphic visual sensors.

Chapter IV

Improvement of experiments

4.1 Reproducibility

A typical disadvantage of thin-film-based-RAM is the lack of protection in the environmentally sensitive switching medium. This problem becomes more severe in organic-inorganic hybrid perovskite RRAMs, as they are subject to moisture attack and rapid degradation,[20] significantly suppressing quality and performance metrics. Therefore, during the experiment, it is necessary to ensure that the quality and performance of materials remain consistent in large-scale production.

At the same time, it is necessary to develop reproducible synthesis and processing processes to ensure the uniformity and reliability of materials. To improve the stability of halide perovskites, approaches such as surface, protective coatings, interface engineering, ionic liquids can be taken. The electronic properties of the material can be modified to improve performance and enhance durability. To make high-quality crystalline perovskite films, considering: Employed THF as a co-solvent in DMF:DMSO precursor solution; Add additives to stabilise the films (eg. Urea.); Introduced liquid medium annealing. Switching linearity in the I-V curve is one of the important factors for high recognition accuracy in neuromorphic computing.[30-31] It is important that the enhancement and suppression of current/resistance be observed reproducibly during the experiment.

In addition, process development and optimization are also important to help improve production efficiency and consistency. After solving the stability of materials and structures, packaging technology suitable for large-scale production can be designed to protect the device and improve its durability. Perform extensive reliability testing to verify the long-term performance of the device under various environmental conditions.

In this experiments, the device needs further experiments and successfully simulates short-term synaptic plasticity, such as paired-pulse facilitation (PPF), and long-term synaptic plasticity (i.e., LTP/STDP), enhancing the reproducibility and stability.

4.2 Ferroelectricity Property

The existence of ion migration within the perovskite layer raises questions regarding whether the ferroelectric synapses observed in halide perovskites stem from factors like polarization reversal or alterations in the orientation of iron domains induced by the ferroelectric properties of the perovskite material. Future experimental endeavors are imperative to ascertain the specific mechanism through which the ferroelectric synapses in devices arise within the active electron layer.

Moreover, it is essential to validate the synaptic linearity of each device and fine-tune the voltage pulse parameters for optimal performance. The goal is to achieve energy consumption per pulse at the picojoule level for Short-Term Plasticity (STP) and Long-Term Potentiation (LTP) operations. The anticipated outcome is that synaptic devices and circuits will exhibit efficient learning capabilities, attaining reasonable accuracy with reduced training cycles.

Ultimately, the culmination of this research aims to demonstrate that ferroelectric DJ-phase halide perovskites harbor the potential for energy-efficient information processing and computing. This work seeks to establish the viability of these materials for driving advancements in efficient and effective computing paradigms.

4.3 Integration & computer sciences

The trend in international development is focused on the advancement of CMOS-compatible memristive materials and the utilization of standard manufacturing processes to create devices. This approach is not only crucial for achieving cost-effective brain-like chips but is also the primary pathway forward. While most implementations of perovskite are confined to dot arrays and crossbar structures, the potential of perovskite brain-computer interfaces can be significantly enhanced through interdisciplinary strategies, leading to the creation of highly efficient and intricate artificial neural circuits.

Integrating perceptron recognition algorithms into these interfaces can enable the simulation of handwriting patterns and the incorporation of multiple layers (input, hidden, and output) to compute and enhance the accuracy of artificial synapses within these simulated patterns. This amalgamation of technologies and methodologies has the potential to drive rapid evolution in perovskite-based brain-computer interfaces, facilitating the development of sophisticated artificial neural networks capable of complex cognitive tasks.

Chapter V

Conclusion

In this research endeavor, a solution-based technique was employed to synthesize two-dimensional Ruddlesden-Popper (RP) out-of-plane ferroelectric perovskite crystals. These crystals serve as ideal candidates for fabricating two-terminal crossbar devices, particularly well-suited for memristor applications within the realm of mimicking biological synapses. These devices possess the capability to emulate neuromorphic learning and memory processes.

The utilization of this perovskite material also introduces the prospect of Dion-Jacobson (DJ) perovskite operating as the active layer in memristor synapses. Concurrently, beyond material exploration, the future applications in this domain hold the potential to propel advancements in areas such as bionic neural network computing and edge computing. This technology harbors immense promise in fostering the development of sophisticated Artificial Intelligence functionalities, including biological simulation and the recognition of animals or humans.

Rreference

[1] Su, T. K., Cheng, W. K., Chen, C. Y., Wang, W. C., Chuang, Y. T., Tan, G. H., ... & Lin, H. W. (2022). Room-temperature fabricated multilevel nonvolatile lead-free cesium halide memristors for reconfigurable in-memory computing. ACS nano, 16(8), 12979-12990.

[2] Li, T., Yu, H., Chen, S. H. Y., Zhou, Y., & Han, S. T. (2020). The strategies of filament control for improving the resistive switching performance. Journal of Materials Chemistry C, 8(46), 16295-16317.

[3] Ren, H., Li, F., Wang, M., Liu, G., Li, D., Wang, R., ... & Zhu, B. An Ion‐Mediated Spiking Chemical Neuron based on Mott Memristor. Advanced Materials, 2403678.

[4] Lee, J., Lee, A. H., Leung, V., Laiwalla, F., Lopez-Gordo, M. A., Larson, L., & Nurmikko, A. (2024). An asynchronous wireless network for capturing event-driven data from large populations of autonomous sensors. Nature Electronics, 7(4), 313-324.

[5] Li, H., Wang, R., Han, S. T., & Zhou, Y. (2020). Ferroelectric polymers for non‐volatile memory devices: a review. Polymer International, 69(6), 533-544.

[6] Weigen, L. (1999). Non-Volatile Ferroelectric Memory and Related Issues. WULI-BEIJING-, 28(4), 216-221.

[7] Vasilopoulou, M., Mohd Yusoff, A. R. B., Chai, Y., Kourtis, M. A., Matsushima, T., Gasparini, N., ... & Noh, Y. Y. (2023). Neuromorphic computing based on halide

perovskites. Nature Electronics, 6(12), 949-962.

[8] Xue, F., He, X., Retamal, J. R. D., Han, A., Zhang, J., Liu, Z., ... & Zhang, X. (2019). Gate - tunable and multidirection - switchable memristive phenomena in a van der Waals ferroelectric. Advanced Materials, 31(29), 1901300.

[9] Li, W., Guo, Y., Luo, Z., Wu, S., Han, B., Hu, W., ... & Wang, H. (2023). A gate programmable van der Waals metal - ferroelectric - semiconductor vertical heterojunction memory. Advanced Materials, 35(5), 2208266.

[10] Cai, Y., Hu, Y., Chen, Z., Jiang, J., Zhang, L., Guo, Y., ... & Shi, J. (2022). Van der Waals ferroelectric halide perovskite artificial synapse. Physical Review Applied, 18(1), 014014.

[11] Fang, Y., Zhai, S., Chu, L., & Zhong, J. (2021). Advances in halide perovskite memristor from lead-based to lead-free materials. ACS Applied Materials & Interfaces, 13(15), 17141-17157.

[12] Chen, L., Pam, M. E., Li, S., & Ang, K. W. (2022). Ferroelectric memory based on two-dimensional materials for neuromorphic computing. Neuromorphic Computing and Engineering, 2(2), 022001.

[13] John, R. A., Milozzi, A., Tsarev, S., Brönnimann, R., Boehme, S. C., Wu, E., ... & Ielmini, D. (2022). Ionic-electronic halide perovskite memdiodes enabling neuromorphic computing with a second-order complexity. Science Advances, 8(51), eade0072.

[14] Park, I. H., Kwon, K. C., Zhu, Z., Wu, X., Li, R., Xu, Q. H., & Loh, K. P. (2020). Self-powered photodetector using two-dimensional ferroelectric Dion – Jacobson

hybrid perovskites. Journal of the American Chemical Society, 142(43), 18592-18598.

[15] Park, I. H., Zhang, Q., Kwon, K. C., Zhu, Z., Yu, W., Leng, K., ... & Loh, K. P. (2019). Ferroelectricity and Rashba effect in a two-dimensional Dion-Jacobson hybrid organic – inorganic perovskite. Journal of the American Chemical Society, 141(40), 15972-15976.

[16] Kalinin, S. V., Rar, A., & Jesse, S. (2006). A decade of piezoresponse force microscopy: progress, challenges, and opportunities. IEEE transactions on ultrasonics, ferroelectrics, and frequency control, 53(12), 2226-2252.

[17] Li, C., Guerrero, A., Huettner, S., & Bisquert, J. (2018). Unravelling the role of vacancies in lead halide perovskite through electrical switching of photoluminescence. Nature communications, 9(1), 5113.

[18] J. M. Azpiroz, E. Mosconi, J. Bisquert, F. De Angelis, Defect migration in methylammonium lead iodide and its role in perovskite solar cell operation. Energ. Environ. Sci. 8, 2118 – 2127 (2015).

[19] Futscher, M. H., Lee, J. M., McGovern, L., Muscarella, L. A., Wang, T., Haider, M. I., ... & Ehrler, B. (2019). Quantification of ion migration in CH 3 NH 3 PbI 3 perovskite solar cells by transient capacitance measurements. Materials Horizons, 6(7), 1497-1503.

[20] Ryu, H., & Kim, S. (2021). Implementation of a reservoir computing system using the short-term effects of Pt/HfO2/TaOx/TiN memristors with self-rectification. Chaos, Solitons & Fractals, 150, 111223.

[21] Cassella, E. J., Spooner, E. L., Smith, J. A., Thornber, T., O'Kane, M. E., Oliver, R. D., ... & Lidzey, D. G. (2023). Binary solvent system used to fabricate fully annealing‐free perovskite solar cells. Advanced Energy Materials, 13(11), 2203468.

[22] Fang, Y., Zhai, S., Chu, L., & Zhong, J. (2021). Advances in halide perovskite memristor from lead-based to lead-free materials. ACS Applied Materials & Interfaces, 13(15), 17141-17157.

[23] Xu, W., Cho, H., Kim, Y. H., Kim, Y. T., Wolf, C., Park, C. G., & Lee, T. W. (2016). Organometal halide perovskite artificial synapses. Adv. Mater, 28(28), 5916-5922.

[24] Cai, Y., Hu, Y., Chen, Z., Jiang, J., Zhang, L., Guo, Y., ... & Shi, J. (2022). Van der Waals ferroelectric halide perovskite artificial synapse. Physical Review Applied, 18(1), 014014.

[25] Xiao, Z., & Huang, J. (2016). Energy-efficient hybrid perovskite memristors and synaptic devices. Advanced Electronic Materials, 2(7), 1600100.

[26] Luo, F., Zhong, W. M., Tang, X. G., Chen, J. Y., Jiang, Y. P., & Liu, Q. X. (2024). Application of artificial synapse based on all-inorganic perovskite memristor in neuromorphic computing. Nano Materials Science, 6(1), 68-76.

[27] Ham, S., Choi, S., Cho, H., Na, S. I., & Wang, G. (2019). Photonic organolead halide perovskite artificial synapse capable of accelerated learning at low power inspired by dopamine‐facilitated synaptic activity. Advanced Functional Materials, 29(5), 1806646.

[28] Chen, S., & Huang, J. (2020). Recent advances in synaptic devices based on

halide perovskite. ACS Applied Electronic Materials, 2(7), 1815-1825.

[29] Chen, J. Y., Tang, X. G., Liu, Q. X., Jiang, Y. P., Zhong, W. M., & Luo, F. (2022). An artificial synapse based on CsPbI3 thin film. Micromachines, 13(2), 284.

[30] Lee, S. U., Kim, S. Y., Lee, J. H., Baek, J. H., Lee, J. W., Jang, H. W., & Park, N. G. (2024). Artificial Synapse Based on a δ-FAPbI3/Atomic-Layer-Deposited SnO2 Bilayer Memristor. Nano Letters, 24(16), 4869-4876.

[31] Huang, W. Y., Zhong, W. M., Chen, J. Y., Liu, Q. X., Jiang, Y. P., Nie, L. H., & Tang, X. G. (2024). Application of multifunctional artificial synapse Cs2AgBiBr6 in pain simulation, Pavlov learning, letter learning and number recognition. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 699, 134629.

[32] Zhang, J., Tsai, H., Nie, W., & Hu, B. (2021). Enabling AC electroluminescence in quasi-2D perovskites by uniformly arranging different-n-value nanoplates to allow bidirectional charge transport. *Nano Energy*, 79, 105413.