Recent Progress in Synaptic Devices Based on 2D Materials

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Diverse synaptic plasticity with a wide range of timescales in biological synapses plays an important role in memory, learning, and various signal processing with exceptionally low power consumption. Emulating biological synaptic functions by electric devices for neuromorphic computation has been considered as a way to overcome the traditional von Neumann architecture in which separated memory and information processing units require high power consumption for their functions. Synaptic devices are expected to conduct complex signal processing such as image classification, decision-making, and pattern recognition in artificial neural networks. Among various materials and device architectures for synaptic devices, 2D materials and their van der Waals (vdW) heterostructures have been attracting tremendous attention from researchers based on their capacity to mimic unique synaptic plasticity for neuromorphic computing. Herein, the basic operations of biological synapses and physical properties of 2D materials are discussed, and then 2D materials and their vdW heterostructures for advanced synaptic operations with novel working mechanisms are reviewed. In particular, there is a focus on how to design synaptic devices with the vdW structures in terms of critical 2D materials and their limitations, providing insight into the emerging synaptic device systems and artificial neural networks with 2D materials.

1. Introduction

The artificial neural network, a biologically inspired computing technology (e.g., deep learning), has had a tremendous influence on science and technology as well as our daily lives. However, state-of-the-art techniques based on artificial neural networks are running with traditional computers based on the von Neumann architecture, leading to long-processing latency and high energy consumption. In contrast with the von Neumann architecture using a separated central processing unit (CPU) and memory part, the neuromorphic computing directly implements memory and complex computations simultaneously in a brain-like fashion. Overcoming the bottleneck of the von Neumann architecture, neuromorphic computing holds promise particularly to handle complex computing issues with high data processing throughput, such as unsupervised learning, associative learning, sound localization, pattern recognition, and so on. Apart from the role for signal transmission among neurons (acting as information hubs) in biological neural systems, the biological synapses conduct information processing by using diverse synaptic plasticity with a wide range of timescales from short term to long term. Long-term changes of synaptic weight provide a physiological platform for learning and memory, whereas short term changes of synaptic weight offer a variety of synaptic computations in temporal domain. In this progress report, we focus on artifical synaptic devices based on 2D materials and van der Waals (vdW) heterostructures, mimicking the short-term plasticity (STP), long-term plasticity (LTP), and the advanced synaptic functions shown in biological synapses.

Synaptic devices require characteristics of a linear conductance response, multiple effective conductance states, and highly stable conductance for each state. At present, synaptic devices using complementary metal oxide semiconductors (CMOS) for artificial intelligence involve numerous transistors and capacitors for a single synapse, making them impractical to mimic the numerous (~10^15) synapses in the human brain. In response, novel electronic and synaptic devices have been demanded to overcome the increasing cost of transistor scaling, as well as the intrinsic inefficiency of using amount of transistors within the architecture of non-von Neumann computing.

Various synaptic devices based on resistive switching, driven by different physical working mechanisms such as active metallic filament, charge trapping/detrapping effect, ions/vacancies migration, phase change behaviors, ferroelectric polarization, and spin-transfer torque-based...
synapses, have been demonstrated for emerging memory and neuromorphic computing. Many scientists are actively working to resolve various issues in those synaptic devices: high energy consumption, low switching speed, poor reliability, or the lack of high device density for integration. We note that they are critical factors for neuromorphic computation.

In active metallic filament devices, the ion migration, involving redox reactions and ion motility, leads to different filament growth modes.\cite{113} The stoichiometric change of the material in the redox process could introduce unwanted impurity-driven doping, which affects the electronic structure of the material.\cite{116,117} In nonfilamentary synaptic devices working by other mechanisms such as charge trapping or detrapping, higher switching uniformity could be obtained. However, the switching behaviors cannot produce a larger dynamic range, limiting the weight linearity and symmetry.\cite{8,118} Phase change materials could demonstrate inherent unipolar switching behaviors because of thermally driven switching mechanisms. Despite their excellent tunable weight and fast switching speed, the phase change consumes a high reset current and power.\cite{119–122} Spin-transfer torque random access memory has advantages with low power consumption for reading and high device density. However, the memory still suffers from the lack of long write latency and large write power.\cite{123,124} Therefore, we note that ongoing studies are struggling to find breakthrough ideas in both materials engineering and understanding of the mechanisms for robust synaptic computation, mimicking massively parallel and practical neuromorphic computing.

Recently, 2D materials have attracted wide interest due to their atomically thin geometry, chemically inert properties, low-dimensional physical properties, and low energy consumption in device operations.\cite{125–128} In particular, 2D materials are feasible to fabricate sub-10 nm channel length device with 2D semiconductor, which could be a way for extending Moore’s law.\cite{139} Ultrathin thickness of channels can facilitate fast heat dissipation and quick response to external stimuli. Moreover, 2D materials can be vertically stacked on arbitrary materials, enabling rich device operations and physics.\cite{126,140–157} The number of reports on 2D materials-based synaptic devices has accordingly increased rapidly. The most representative 2D materials in the aforementioned are graphene\cite{158–161} transition metal dichalcogenides (TMDs) (e.g., MoS\textsubscript{2}\cite{11,18,162–166} and WSe\textsubscript{2}\cite{167}), black phosphorus (BP),\cite{168} hexagonal boron nitride (h-BN),\cite{6,165,169–172} and various vdW heterostructures with these 2D materials.\cite{173–176}

Together with the inorganic 2D materials, 2D organic layers have attracted the attention of researchers because the solution-based process and flexibility in 2D organic layer materials enable low fabrication cost for large-area production. In particular, 2D organic molecules modulate the response to external signals, providing a potential platform for realizing sensory synapses in multidimensions.\cite{176–178}

Based on the negligible volume of 2D materials, synaptic operation by tens of femtojoule per spike has been realized widely,\cite{11,179,180} which is comparable with the energy consumption per spike in biological synapses.\cite{181} However, the disadvantages of 2D materials have also been revealed: limited synthesis methods for wafer-scale geometry\cite{147,182} and the lack of compatibility to CMOS fabrication processes.\cite{183,184} This progress report will review the 2D materials library and state-of-the-art fabrication methods. Then, original working mechanisms in 2D material-based synaptic devices will be explained. Finally, the opportunities and challenges with 2D material-based synaptic devices will be discussed.

\section{2. Synaptic Plasticity for Neuromorphic Computing}

A neuron connected with thousands of synapses through active dendrites can recognize hundreds of independent patterns of cellular activity.\cite{185,187–189} Synapses transmit biological spike signals between the neurons with synaptic plasticity; the transmitted information highly depends on the recent history of the spiking activity at either or both sides of the synapses.\cite{189} Depending on the function of neurotransmitter receptors on the synaptic membrane, synapses are divided into two categories: excitatory and inhibitory synapses.\cite{186,190–193}
The activity-dependent variations in the synapse signal transmission are related to many transmission mechanisms.\textsuperscript{186} Based on the timescales of the activity variations of synaptic plasticity can be again classified into two main types: 1) short-term synaptic plasticity (STSP), 2) long-term synaptic plasticity (LTSP). By balancing the potentiation and depression functions of the cerebral cortex in the short term, STSP enhances the synaptic transmission in a controllable manner, realizing the temporal and spatial characteristics of neural activity.\textsuperscript{13,194} LTSP refers to the changes lasting for hours or longer.\textsuperscript{195–200} Similar to potentiation and depression functions in STSP, LTSP consists of long-term potentiation (LTP) and long-time depression (LTD),\textsuperscript{201,202} which have been widely known as the biological basis for long-term learning and memory.

Concerning the relative timing of the pre- and postsynaptic signals or the action potentials for Hebbian rules,\textsuperscript{203–205} spike-timing-dependent plasticity (STDP) has been widely investigated.\textsuperscript{204,206–208} It has been found that STDP can realize unsupervised learning by tuning the connection strengths between pre- and postsynaptic neurons.\textsuperscript{209} Depending on the relationships between the synaptic weight changes and pulse time intervals, the STDP can be classified into four types,\textsuperscript{210–212} as shown in Figure 1: 1) asymmetric Hebbian STDP learning process, 2) asymmetric anti-Hebbian STDP learning rule (original STDP), 3) symmetric Hebbian rule, and 4) symmetric anti-Hebbian rule. Briefly, the symmetry of the learning rule is critical to determine the characteristics of the stored memory and to generate stable memory with newly appended information, for example, an asymmetric learning rule could generate flexible (volatile) memory that can be overwritten easily by newly appended information. The Hebbian learning rules are the basis of unsupervised learning processes. Thus, extensive efforts have been made to mimic the synaptic functions by electronic (synaptic) devices.

3. Library of 2D Materials and Their Heterostructures

The most widely studied 2D material is graphene due to its exceptionally wide ranges of applications in optoelectronic, electrochemical, mechanical, and biomedical fields.\textsuperscript{213–218} After graphene, diverse 2D materials have been explored because of their unique properties in polymorphism, spin–orbit coupling, and so on.\textsuperscript{141,219–225} Figure 2a shows the library of 2D materials exhibiting a list of possible monolayers of the materials.\textsuperscript{141} The background colors show their stabilities in ambient and vacuum. The 2D insulators supply an ultra-flat dielectric layer in the electrochemical metallization/conductive bridge-based resistance switching devices,\textsuperscript{6,171} as well as the barrier of tunneling effect-based synaptic devices.\textsuperscript{179}

2D semiconductors, due to their rich physical properties in spintronics, valleytronics, and phase changing,\textsuperscript{226} could mimic synaptic devices by their unique properties such as spin-transfer torque, phase change, joule heating, and so on. On the contrary, 2D oxides, including TiO$_2$, MoO$_3$, WO$_3$, and so on in the table, are mostly not stable in air because the materials possess many oxygen vacancies, which could be used to demonstrated synaptic devices with ion migration/oxygen vacancy, charge trapping/detrapping, and so on. Apart from the explored 2D materials shown in Figure 2a,b, many layered materials fabricated by stacking different 2D materials in a “Lego” manner exist (Figure 2c). Combining different 2D materials matching their electronic properties, tunable barrier heights could be used for diverse synaptic strengths.\textsuperscript{173}

Various methods have been developed to synthesize 2D materials: mechanical exfoliation, liquid exfoliation, wet chemical synthesis, and vapor phase chemical reactions.\textsuperscript{227–231} By mechanical exfoliation, it is difficult to obtain large-scale monolayer 2D materials for synaptic device integration, although this fabrication method provides high crystal quality. By liquid
exfoliation methods or wet chemical synthesis methods, various 2D flakes could be prepared in mass production; however, external ions or compounds are inevitable involved in the synthesis, and the domain size of the 2D materials ranges from only tens to hundreds of nanometers. Moreover, the thicknesses, morphology, and size of flakes are difficult to control.[232–236]

Chemical vapor deposition (CVD) has been widely used for highly scalable films of crystals.[237–240] Another technique to grow high-quality 2D materials is molecular beam epitaxy (MBE).[241–243] MBE realizes accurate control of the thickness, and enables the epitaxial growth of 2D materials on certain substrates but with inefficient production speed. Recently, metal-organic chemical vapor deposition (MOCVD) with gas phase precursors has been developed to grow large-scale 2D TMDs.[244,245] Despite the scalable and uniform 2D materials by various CVD methods, inevitable limitations, such as natural defects during the synthesis process, still prevent practical applications. The lacking of proper synthesis methods of 2D materials is one of the biggest issues in developing 2D electronics and synaptic devices based on 2D materials.

4. 2D Materials and Heterostructure-Based Synaptic Devices

Various 2D material-based optoelectronic devices for emulating biological synapses have been explored recently, and they can be classified into their working mechanisms: metallic ion/electrochemical metallization/conductive bridge, ion migration/oxygen vacancy, modulation of chemical valence, charge trapping/detrapping, phase change transition, resistive heating, ionic gating, tunneling effects, organic 2D molecular layer, and vdW architecture. The details of each type of synaptic devices are described later.

4.1. Metal Ion Migration/Conductive Bridge Filaments

In 2010, a two-terminal synaptic device, analogous to the structure of a typical memristor, was developed with a Si/Ag thin film by Lu and co-workers.[238] Similar to the working mechanism of a memristor, the synaptic weight or conductance of the synaptic device varies by the active metal (Ag, Cu, W, etc.) ion migration...
upon external electrical stimuli, realizing synaptic behaviors, such as potentiation, depression, and STDP.\textsuperscript{[19,29–33,35,37–40]} Moreover, the crossbar structure of memristors lends this type of synaptic device promise for high-density integration.

Thus far, the previously reported memristive synaptic devices can be classified into two types with distinct device structures: 1) gradually distributed of metal ions or clusters in the semiconductor or insulator layer,\textsuperscript{[30,246,247]} 2) metallic ions generated only from the redox reactions at the interface between the active electrode and switching layer over a threshold voltage bias.\textsuperscript{[19,32]} Recently, due to their unique stability and functionalities, 2D material-based memristive synaptic devices have been extensively reported, as shown in Figure 3. Feng et al. reported an aerosol-jet-printed Ag/MoS$_2$/Ag memristive synapse in a crossbar structure.\textsuperscript{[165]} Both STSP and LTSP were demonstrated. An ultralow switching voltage (0.18 V), low power consumption (1 fW), a high switching ratio ($10^7$), and a wide range of resistance states ($10^{15}$–$10^{10}$ Ω) for multibit information storage were demonstrated, revealing its promise to mimic integrated energy-efficient neuromorphic computing.

Other insulating 2D materials such as h-BN also have been used for enhancing memristive behavior. For instance, filling/depleting the boron vacancies with metal ions from an active electrode to form/rupture a conductive bridge led to volatile and nonvolatile resistance switching (or between STSP and LTSP) of electrical synapses.\textsuperscript{[170,171]} A new class of 2D vdW materials, TmPS$_x$, where Tm represents a transition metal, was sandwiched by Ag and Au electrodes to demonstrate multiple resistance states for synaptic devices using voltage bias smaller than 0.3 V.\textsuperscript{[248]}

Moreover, the strong in-plane bonding in 2D materials can mitigate the ubiquitous variation issues. Recently, Zhao and co-workers reported a device with a subnanometer switching layer thickness (BN oxide material: BNO$_x$) by oxidizing 2D h-BN.\textsuperscript{[169,249]} Such a subnanometer filament layer (0.9 nm) demonstrates a switching current with several picoampere and energy consumption of several femtojoule per bit. The atomistic chain filaments in the aggressively scaled device allows the realization of ultralow power operation and fast switching speed, compared with former devices. The switching mechanism

![Figure 3](https://www.advancedsciencenews.com/)

**Figure 3.** Flexible MoS$_2$ memristive artificial synapse with Ag metallic ion diffusion. a) Schematic of the Ag/MoS$_2$/Ag memristor with a $4 \times 4$ crossbar structure on a flexible substrate (polyimide). b) The proposed diffusion paths of Ag ions and their corresponding energy barriers. c) Thickness of MoS$_2$-dependent variations of the filament quantity with time. d) Synaptic potentiation stimulated by sequence of pulse train, with pulse width and interval of 50 and 100 μs, respectively. e) The relaxing dynamic processes with a short pulse width and period of 100 and 900 μs. The setting and reading voltages are 1 and 0.1 V, respectively. f) The series of pulses train enables demonstration of progressive LTP. g) Progressive long-term depression LTD. Reproduced with permission.\textsuperscript{[165]} Copyright 2019, Wiley-VCH.
benefits the realization of the memristive electronics at an energy level of subfemtojoule per bit, and promises many emerging applications such as binary synapses in neuromorphic computation networks. In summary, 2D material-based memristive synaptic devices with metallic ion migration have been demonstrated energy-efficient next-generation, flexible neuromorphic technologies.

4.2. Anion Migration

Conventional memristor technology adopts a binary switching mechanism based on a distinct low resistance state (LRS) and high resistance state (HRS), which is a primary limitation for synaptic device applications. More seriously, the inherent working mechanism leads to variation of conductive paths formed by metal ion filaments, especially for low current operation (by unstable paths), which leads to a stochasticity or uniformity issue for resistance tuning. Tian et al. reported another class of 2D materials, as shown in Figure 4: perovskite single crystals, for ultralow operation current of 10 pA using the migration of bromide ions. The elemental density profiling and transmission electron microscopy (TEM) images support the mechanism of Br⁻ ion migration and reveal the diameter of filament to be ≈20 nm. The 2D perovskite crystals supply a sufficient ionic transport ability (or ionic mobility) with limited electron transport ability (i.e., electron mobility), which overcomes the bottleneck of high leakage current from defect-mediated oxygen ion migration in previous resistive switching devices. As shown in Figure 4, a positive pulse bias drives Br⁻ toward the Au electrode, and a negative bias pulse drives Br⁻ back to the Br⁻ vacancies, resulting in enhancement or recovery of the conductance of the channel, corresponding to the STSP in a biological synapse. Furthermore, multiple pulses trains could completely drive the formation of a robust filament, demonstrating long-term memory behaviors for longer than 1000 s.

Figure 4. 2D perovskite single crystal-based synapse via the migration of bromide ions. a) Schematic illustration of device structure with graphene/2D perovskite/Au substrate. The zoomed-in area shows the atomic structure of the channel material. b,c) Working mechanisms of a biosynapse and 2D perovskite-based artificial synapse, respectively. d) The postsynaptic current (PSC) response to different voltage stimulus. e) Synaptic potentiation and f) depression function induced by positive and negative peak current pulses. g) Two positive pulse induced potentiation following the former negative pulse induced depression. h) STP stimulated by six pulses train. i) The device switched to LTP by a second round of six pulses. Reproduced with permission. Copyright 2017, American Chemical Society.
4.3. Valence Change by Proton Doping

Distinguished from the electrochemical memory cells involving the electrochemical reactions of metals and ion migration, the valence change of the elements in 2D materials for some synaptic devices originates from the migration of protons/oxygen vacancies in the switching layers. In the 2D material-based synaptic devices, both electrical and optical stimuli could lead to a valence change of the channel materials.

Yang et al. reported a solid-state memristive synaptic device with electrochemical redox reactions in MoOx thin film in 2017.[251] The interfacial electrochemical reaction of the MoOx film with the adsorbed water molecules contributes to the switching of the synaptic device. By increasing the gate voltage, the protons produced from the decomposition of water can intercalate into the oxide lattice and change the ion state from Mo$^{6+}$ to Mo$^{5+}$, with the formation of molybdenum bronze (H$_3$MoO$_3$). On the contrary, a negative gated voltage can extract the protons from the channel materials and recover the valence state. Recently, Chai’s group revealed that a UV laser (365 nm) with a certain power density could switch the MoO$_x$-based memristive device to LRS from HRS, as shown in Figure 5.[252] The photo-generated electrons and the protons can change the valence states of the Mo ions (from 6$^+$ to 5$^+$). Or, specifically, the reset voltage can drive the protons moving toward the Pd electrode to recover the valence state of Mo ion back to 6$^+$, leading to the transition of resistance states in the device. Such an optoelectronic resistive random access memristive device with the ability to respond to optical stimuli directly provides a platform for the application of a neuromorphic visual system by simplifying the circuitry and lowering the energy consumption. The UV light used in this work also enables an artificial visual system beyond the visible light region of human beings.

4.4. Charge Trapping/Detrapping

In contrast with the devices based on metal-ion filaments or ion/vacancy migration accompanying structural changes of dielectric layers, synaptic devices based on charge trapping and detrapping operate in a purely electronic way without any microstructure change. As the ion-induced structural change leads to unavoidable variation of device performance, the charge trapping and detrapping synaptic devices have been considered promising over the ion-based devices in terms of reliability.[253] In recent years, memristive devices based on charge trapping and detrapping diverse materials, such as MoO$_x$/GdO$_x$, Nb$_2$O$_5$, CeO$_2$, and Ge$_2$Sb$_2$Te$_5$, have been actively investigated.[45,254–257]

With an accompanying increasing research in 2D materials, a number of research groups have reported works utilizing graphene and other 2D materials in volatile and nonvolatile memory.[15,158,362,164,177,178] Arnold et al. reported a synaptic device through engineering of hysteresis in MoS$_2$ transistors to mimic the key functions in a chemical synapse.[162] With adsorbates such as oxygen and water molecules on the surface of MoS$_2$, the negative gated voltage drives the release of electrons from the trapping states into the MoS$_2$, whereas the positive gated voltage depletes electrons from the MoS$_2$. By operating with suitable frequency, amplitude, and polarity of gate voltage pulses, the devices demonstrate essential functions of neurotransmitter release in a chemical synapse.

However, such charge trapping/detrapping from the interface between adsorbates and channel materials highly depends on the ambient conditions. Seo et al. reported a vdW synaptic device based on charge trapping/detrapping in h-BN/WSe$_2$ heterostructure (Figure 6).[15] The synaptic weights could be modified by charge trapping in the switching layer that is formed on h-BN treated by O$_2$ plasma irradiation. The synaptic device operates with a low spike amplitude of 0.3 V and a low energy consumption of 66 fJ per spike. Moreover, the integration of the synaptic devices demonstrated diverse synaptic functions such as LTP, LTD, and STDP by both electrical and optical stimuli. Colored and color-mixed pattern recognition in human vision system thus could be emulated, paving the way to realize neural sensing and training systems for complex and practical pattern recognition.

4.5. Phase Change Materials

Phase change materials have been used as nonvolatile resistance switching layers in memristors since 1968.[258] These memristors switch their states between amorphous and crystalline states for the on and off states. The major advantages of the phase change materials for memristors are reliability, durability, and scalability.[82,84,86,87,89] The most typical phase change materials are chalcogenide glasses that allow optical data storage, nonvolatile memory, and artificial synaptic devices.[86] Recently, various methods for phase change engineering with 2D materials have been reported by using laser/plasma/electron irradiation, chemical intercalation, and so on.[85,257,259–262]

Beyond nonvolatile memory applications, mimicking synaptic devices and neuromorphic computation have been demonstrated with phase change materials. Zhu et al. reported a reversible local phase transition between a 2H semiconductor and 1T metal phase in MoS$_2$ by controlling the migration of Li$^+$ ions under an electric bias voltage, as shown in Figure 7.[83] The redistribution of Li$^+$ ions by voltage application leads to a local phase transition near the electrodes. The easy diffusion of Li$^+$ ions produced memristive behaviors in their study. The authors also demonstrated effective ionic coupling among multiple synaptic devices based on MoS$_2$, which means the potentiation of one synaptic device can facilitate the potentiation of a neighboring synaptic device (Figure 7b–g). This work provides a way to mimic the synaptic competition and cooperative effects in complex biological neural networks.

Huh et al. demonstrated a synaptic barristor based on a phase engineered heterojunction of tungsten oxide/selenide monolithic.[174] The synaptic devices with phase-engineered 2D materials realize important synaptic functions such as STP, LTP, and paired-pulse facilitation (PPF) with a low power consumption, shedding light on the implementation of highly integrated, energy-efficient neuromorphic circuits.

4.6. Joule Heating Effect for STP

Heat is generated and released when an electric current flows through a conductor/semiconductor channel, which is called
Figure 5. Optoelectronic resistive random access memory (RRAM) for neuromorphic vision sensors. a) The proposed working mechanism for resistance switching in the MoO$_x$, based on the valence state change of Mo$^{5+}$ (green balls) and Mo$^{6+}$ (blue balls). b) Modulation of STP by various light intensity with a pulse width of 200 ms. c) Illustration of the human visual system. d) Artificial neuromorphic vision sensors for image preprocessing, and an artificial neural network for image recognition. e) Comparison of images before (left columns) and after (right columns) preprocessing. f) Comparison of the image recognition rate with and without image preprocessing. Reproduced with permission.\textsuperscript{[252]} Copyright 2019, Springer Nature.
Joule heating. The amount of the heat and its release by joule heating can be tuned by the conductivity of materials. Compared with other working mechanisms, the change of conductance driven by joule heating demonstrates monostable conductance threshold switching. Once a bias voltage lower than a certain threshold is applied for the joule heating, the conductance of the channel materials would soon recover the original value due to the release of heat (cooling down).

Recently, a two-terminal device with a single-layered MoS$_2$ channel demonstrated synaptic behaviors including both synaptic potentiation and depression by using the joule heating effect (Figure 8). Excitatory and inhibitory synaptic devices could be achieved by the negative and positive temperature–resistivity relation in a semiconducting and metallic MoS$_2$ monolayer, and such metal–insulator transitions have been reported in multiple 2D materials. The characteristic times of the synaptic plasticity can be controlled by versatile doping effects in the MoS$_2$ monolayer (Figure 8d). While the operation energy critically depends on the dimension of the device, an operating energy per spike of 10 fJ has been demonstrated.

The integration of excitatory and inhibitory synaptic devices, together with a peripheral circuit, realizes key functions in sound localization including efficient detection of interaural time differences (Figure 8f,g). The electric gating to induce a
metallic and semiconducting MoS\(_2\) monolayer (requiring three-terminal devices) could be replaced by a material synthesis with controllable carrier concentrations, which achieves selective (potentiation and depression) synaptic information transmission in a two-terminal device architecture. These studies provide a breakthrough for complex synaptic networks to mimic the sophisticated and precise synaptic information processing in the brain, potentially resolving the issues of the scalability and high power consumption in conventional CMOS-based synaptic device technology.

### 4.7. Ionic Gating for Synaptic Devices

Synaptic devices in a geometry of three-terminal transistors using 2D materials have demonstrated promising energy consumption and atomically thin device geometry. In contrast with conventional electrostatic gating, ionic gating using an electrolyte has been suggested as an alternative way to realize an efficient artificial synapse. The ionic gating uses the electric double layer (EDL) capacitance, which decreases the gate voltage and energy consumption and implements unique synaptic functions by integrated electric and photo stimuli; bidirectional excitatory/inhibitory postsynaptic currents and their corresponding PPF/paired-pulse depression (PPD) have been demonstrated. Although a working mechanism with charge trapping/detrapping is similarly involved in the ionic-gating device, we describe this in a separated section in this review due to its unique properties.

MoS\(_2\), as a representative 2D material, has been used to build a multifunctional, photoelectronic hybrid synaptic device. Synaptic potentiation and depression are achieved by an electric current and a photo current, respectively, as shown in Figure 9. [83] Copyright 2019, Springer Nature.
Both non-Hebbian and Hebbian rule-based learning were emulated, which enables 4D degree of information processing (photoelectric and spatial–temporal hybrid data processing).

Apart from MoS$_2$, other 2D layered molybdenum oxides also showed similar synaptic dynamics with a comparable operation energy.$^{[251]}$ It is still a challenge to achieve reliable, large-scale integration using in-plane ionic gating. Moreover, ionic liquid gating has difficulties to emulate LTSP due to the short characteristic times related to most liquid electrolytes. In addition, the possible electrochemical reactions in the gating process could modify the successive concentrations of ions and thus the synaptic device operation, particularly in ambient conditions. Therefore, further efforts should be made to meet the critical demands of reliability and high-integration architecture required for optoelectronic computation beyond CMOS electronics.

4.8. Tunneling Effect

Floating gate memory devices have been widely explored in CMOS architecture, and the charge tunneling between the floating gate and the channel enables the storage function of information.$^{[272,273]}$ Due to the unique properties of 2D materials, there is potential to stack different vdW layered materials together in an atomic “Lego” manner, in which one metallic layer could act as the floating gate for temporary charge storage enabled by a back or top gate. However, despite a considerable body of work on the implementation of diverse floating gate memory devices, the current device structures of floating gate memory with 2D materials are unprofitable for realistic neuromorphic applications in hardware due to the large gate voltage involved, leading to high energy dissipation per pulse.

Figure 8. Synaptic computing enabled by joule/resistive heating in a single-layered 2D semiconductor. a) Schematic of two-terminal synaptic devices with joule heating effect in monolayer MoS$_2$ channel. b,c) Simulations of temperature evolutions induced by joule heating in monolayer MoS$_2$, after the pulse stimulated with amplitude of 5 V and width of 100 ms. Part (b) represents heating process and part (c) shows the cooling down process. d) Gate–voltage-dependent STP and time scales (Normalized data). e) The interpulse interval-dependent PPF and PPD indexes after stimulation by two consecutive pulses. f) Schematic diagrams for sound localization with competing interaural time difference (ITD) and interaural level difference (ILD) processes. g) The working mechanism of synaptic computation for only ITD-based sound localizations. Reproduced with permission.$^{[13]}$ Copyright 2018, American Chemistry Society.
Paul et al. successfully improved the efficiency of gating, leading to a quasi-ideal subthreshold swing (77 mV per decade) and reduction of the required drain bias and switching pulse, by using an extend graphene floating gate, as shown in Figure 10a,b. An h-BN layer, working as tunneling barrier, separates the floating gate and channel, which could control the charge transfer and tune the conductance of the channel for mimicking the synaptic plasticity (Figure 10c–e). Neuromorphic computations, including long-term synaptic potentiation, depression, and STDP, have been realized based on this architecture in a smaller pulse amplitude (Figure 10d,f,g) emulating STDP at energy dissipation of ≈5 fJ. This is conducive for improving the integration of the device due to the reduction of stress on the gate dielectric based on current neuromorphic systems. This work provides a new and robust platform for mimicking solid-state synaptic devices free of electrochemical reactions and defects/ion migration, offering potential for future integrated neuromorphic applications.

4.9. vdW Heterostructures

Normally, whether a synapse’s function is excitatory or inhibitory is determined from the types of ion migration channels in the postsynaptic neurons stimulated by the neurotransmitter released from the presynaptic neuron, and this can be mimicked by 2D materials. However, a recent study revealed the event of coreleasing excitatory and inhibitory neurotransmitters, which allows both postsynaptic potentials to occur at a synapse in the lateral habenula, even in certain neurons with GABA neurotransmitters in mammalian brain’s synaptic activities, which is difficult to be mimicked by 2D materials. It is necessary...
to make a same synaptic device to have both excitatory and inhibitory functions with desired flexibility and versatility overcoming the conventional single synaptic unit including numerous transistors at the circuit level.

VdW heterostructures possess rich physics that could be used for demonstrating specific electronics. Tian et al. proposed an artificial synaptic architecture with both excitatory and inhibitory operation by using a tunable heterostructure stacked with BP and tin selenide, as shown in Figure 11a. In contrast with previous heterosynaptic devices that require a third active terminal to tune the synaptic weight, the synaptic behaviors could be dynamically modulated by only the input and output bias in the device (Figure 11b). Some key synaptic functions, such as potentiation, depression, and STDP, could be mimicked (Figure 11c–f), offering a promising architecture to mimic synaptic reconfiguration in biological neural networks.
5. Comparison of Different Synaptic Devices

We have investigated nine different types of 2D material-based synaptic devices that have been reported so far. To clearly summarize their pros and cons, we chose key parameters and functions in the different working mechanisms that are vital to mimic diverse neural networks, as shown in Table 1.

Both STSP and LTSP could be mimicked by the working mechanisms based on conductive filaments (e.g., metal ion or anion migration). The device structures with a single active electrode (or asymmetric device structures) could demonstrate STP and LTP (part 4.1–4.3), whereas biactive electrodes (or symmetric device structures) could demonstrate both potentiation and depression (part 4.1). We note that the filament-based synaptic

Table 1. Comparison of key parameters and functions among different synaptic devices.

| Types of synaptic device         | STP/STD | LTP/LTD | Endurance (for LTP and LTD) | Retention (for LTP and LTD) | Operating power per spikes | Multilevel states | Availability of light stimuli | References |
|---------------------------------|---------|---------|-----------------------------|-----------------------------|---------------------------|---------------------|-----------------------------|------------|
| Metal ion migration             | Only STP| LTP/LTD | –                           | >11 h for LTP               | 4.5 fJ                   | Yes                 | No                          | [165]      |
| Anion migration                 | Only STP| Only LTP| 100 cycles                 | >1000 s                     | 400 fJ                   | Yes                 | No                          | [249]      |
| Valence change by proton doping | Only STP| Only LTP| 12 cycles                  | >24 h                       | –                        | Yes                 | Yes                         | [251]      |
| Charge trap/detrap              | No      | LTP/LTD | –                           | –                           | 66–532 fJ                | Yes                 | Yes                         | [15]       |
| Phase change effect            | No      | LTP/LTD | 10^2 cycles                | >7000 s                     | ≈3.6 nJ                  | No                  | No                          | [83]       |
| Joule heating effect            | STP/STD | No      | No                          | No                          | 72 fJ                    | Yes                 | No                          | [13]       |
| Ionic gating                    | STP/STD | No      | No                          | No                          | 300 pJ                   | Yes                 | Yes                         | [262]      |
| Tunneling effect                | No      | LTP/LTD | ≈10^3 cycles               | >3500 s                     | <5 fJ                    | Yes                 | No                          | [178]      |
| Van der Waals heterostructures  | STP/STD | No      | –                           | –                           | 6–150 nJ                 | Yes                 | No                          | [172]      |
devices mostly require large forming voltages to activate the device channel\cite{16,17} despite their low operation voltage and power consumption (part 4.1–4.3). Moreover, by setting various compliance current levels, multilevel resistance states could be achieved (part 4.1–4.3).

The filament-based synaptic devices are insensitive to optical stimuli (part 4.1–4.2). However, the unique properties of 2D semiconductor materials, such as light-driven doping\cite{252} charge trapping/detrapping by light illumination\cite{277} or light-induced phase transition\cite{259} provide another dimension for synaptic operation: sensitivity to optical stimuli\cite{252}. The lack of sensitivity to light stimuli in part 4.5 originates from the phase transition by ion intercalations rather than light illumination\cite{83}.

Regarding joule heating effect-based synaptic devices, heat dissipation in ultrathin 2D materials is a key factor to demonstrate LTP and LTD. Ionic-gated three-terminal devices, where highly sensitive electrolyte should be used, require high gate voltages, which makes the device performances unstable. Tunneling effect-based synaptic devices have demonstrated low currents and fast switching speeds, thus ultralow power consumption\cite{179}. However, the working mechanism cannot realize STP. Lastly, vdW heterostructures could tune the synaptic weight\cite{173} depending on the band alignments by stacking materials; however, the fabrication of the heterostructures is not scalable yet and involves unavoidable defects or surface states at the interfaces, which increases the risk of performance variations.

6. Conclusion

2D materials and their vertical heterostructures provide novel and diverse working mechanisms for synaptic devices that can be eventually integrated for neuromorphic computation. Although great progress has been achieved to date, we are still far away from the realization of system-level, brain-inspired neural computing for practical artificial intelligence. Two critical concerns with 2D materials should be addressed for further applications: 1) wafer-scale synthesis of high-quality and uniform 2D materials and 2) their compatibility with traditional CMOS fabrications.

All previous studies on synaptic computation systems with 2D materials have demonstrated performance with only a few or tens of synapses or neurons and powerful simulations. It is still quite challenging to develop proper fabrication processes for 2D materials-based electronic devices using conventional semiconductor technology. Another important issue with 2D materials for synaptic applications is the reliability. The crystal quality of 2D materials, a key factor for desired synaptic operations, varies according to the various synthesis conditions or growth methods from lab to lab. The reliability of 2D materials-based synaptic devices has been underestimated in past studies. Breakthroughs for the synthesis of wafer-scale, uniform, and high-quality atomically thin films for largely integrated synaptic and neuron devices in the compatibility with traditional CMOS process will push the development of practical and promising neuromorphic computing.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

artificial neural networks, synaptic device integration, synaptic plasticity, van der Waals heterostructures, 2D materials

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[1] J. Pei, L. Deng, S. Song, M. Zhao, Y. Zhang, S. Wu, G. Wang, Z. Zou, Z. Wu, W. He, F. Chen, N. Deng, S. Wu, Y. Wang, Y. Wu, Z. Yang, C. Ma, G. Li, W. Han, H. Li, H. Wu, R. Zhao, Y. Xie, L. Shi, Nature 2019, 572, 106.

[2] Z. Wang, M. Rao, J.-W. Han, J. Zhang, P. Lin, Y. Li, C. Li, W. Song, S. Asapu, R. Midya, Y. Zhuo, H. Jiang, J. H. Yoon, N. K. Upadhyay, S. Joshi, M. Hu, J. P. Strachan, M. Barnell, Q. Wu, H. Wu, Q. Qiu, R. S. Williams, Q. Xia, J. Y. Yang, Nat. Commun. 2018, 9, 3208.

[3] Z. Wang, C. Li, P. Lin, M. Rao, Y. Nie, W. Song, Q. Qiu, Y. Li, P. Yan, J. P. Strachan, N. Ge, N. McDonald, Q. Wu, M. Hu, H. Wu, R. S. Williams, Q. Xia, J. Y. Yang, Nat. Mach. Intell. 2019, 1, 434.

[4] Z. Wang, C. Li, W. Song, M. Rao, D. Belkin, Y. Li, P. Yan, H. Jiang, P. Lin, M. Hu, J. P. Strachan, N. Ge, M. Barnell, Q. Wu, A. G. Barto, Q. Qiu, R. S. Williams, Q. Xia, J. Y. Yang, Nat. Electron. 2019, 2, 115.

[5] F. Cai, J. M. Correll, S. H. Lee, Y. Lim, V. Bothra, Z. Zhang, M. P. Flynn, W. D. Lu, Nat. Electron. 2019, 2, 290.

[6] L. Sun, Y. Zhang, G. Han, C. Hwang, J. Jiang, B. Joo, K. Watanabe, T. Taniguchi, Y.-M. Kim, W. J. Yu, B.-S. Kong, R. Zhao, H. Yang, Nat. Commun. 2019, 10, 3161.

[7] J. Feldmann, N. Youngblood, C. D. Wright, H. Bhaskaran, W. H. Pernice, Nature 2019, 569, 208.

[8] J. Wang, F. Zhuige, Adv. Mater. Technol. 2019, 4, 1800546.

[9] A. M. Zador, Nat. Commun. 2019, 10, 3770.

[10] C.-C. Chen, H.-H. Juan, M.-Y. Tsai, H. H.-S. Lu, Sci. Rep. 2018, 8, 557.

[11] M. C. Klein-Flügge, M. K. Wittmann, A. Shpekter, D. E. A. Jensen, M. F. S. Rushworth, Nat. Commun. 2019, 10, 4835.

[12] E. O. Nefci, B. B. Averbeck, Nat. Mach. Intell. 2019, 1, 133.

[13] L. Sun, Y. Zhang, G. Hwang, J. Jiang, D. Kim, Y. A. Eshele, R. Zhao, H. Yang, Nano Lett. 2018, 18, 3229.

[14] W. Wang, G. Pedretti, V. Milo, R. Carboni, A. Calderoni, N. Ramaswamy, A. S. Spinelli, D. Ielmini, Sci. Adv. 2018, 4, eaat4752.

[15] S. Seo, S.-H. Jo, S. Kim, J. Shim, S. Oh, J.-H. Kim, K. Heo, J.-W. Choi, C. Choi, S. Oh, D. Kuzum, H. S. P. Wong, J.-H. Park, Nat. Commun. 2018, 9, 5106.

[16] G. C. Adam, A. Khiat, T. Prodromakis, Nat. Commun. 2018, 9, 5267.

[17] L. F. Abbott, W. G. Regehr, Nature 2004, 431, 796.
[35] L. Hu, S. Fu, Y. Chen, H. Cao, L. Liang, H. Zhang, J. Gao, H. Cao, B. Fu, K. Li, Appl. Phys. Lett. 2016, 108, 013504.
[36] Y. Li, Y. Zong, L. Xu, J. Zhang, X. Xu, H. Sun, X. Miao, Sci. Rep. 2013, 3, 1619.
[37] S.-R. Zhang, L. Zhu, J.-Y. Mao, Y. Ren, J.-Q. Yang, G.-H. Yang, X. Zhu, S.-T. Han, V. A. L. Roy, Y. Zhou, Adv. Mater. Technol. 2019, 4, 1800342.
[38] J. Choi, E. Park, J. Woo, K. Kwon, IEEE Electron Device Lett. 2019, 40, 1848.
[39] A. S. Sokolov, Y.-R. Jeon, S. Kim, B. Ku, C. Choi, NPC Asia Mater. 2019, 7, 5.
[40] M. Kumar, S. Abbas, J. Kim, ACS Appl. Mater. Interfaces 2018, 10, 34370.
[41] Y.-N. Zhong, X. Gao, J.-L. Xu, H. Siringhans, S.-D. Wang, Adv. Electron. Mater. 2019, 6, 1900055.
[42] Q. Wu, H. Wang, Q. Luo, W. Banerjee, J. Cao, X. Zhang, F. Wu, Q. Liu, L. Li, M. Liu, Nanoscale 2018, 10, 5875.
[43] K. Seo, I. Kim, S. Jung, M. Jo, S. Park, J. Park, J. Shin, K. P. Biju, J. Kong, K. Lee, B. Lee, H. Hwang, Nanotechnology 2017, 22, 254023.
[44] W. Banerjee, W. F. Cai, X. Zhao, Q. Liu, H. Lv, S. Long, M. Liu, Nanoscale 2017, 9, 18908.
[45] J. Woo, K. Moon, J. Song, S. Lee, M. Kwak, J. Park, H. Hwang, IEEE Electron Device Lett. 2016, 37, 994.
[46] D. Garbin, O. Bichler, E. Vianello, R. Rafayh, C. Gamrat, L. Perniola, G. Chibaudo, B. Desalvo, presented at IEEE Int. Electron Devices Meeting, San Francisco, CA, December 2014.
[47] S. Yu, Y. Wu, R. Jeyasingh, D. Kuzum, H. P. Wong, IEEE Trans. Electron Devices 2011, 58, 2729.
[48] M. J. Rozenberg, M. J. Sánchez, R. Weht, C. Acha, F. Gomez-Marlasca, P. Levy, Phys. Rev. B 2010, 81, 115101.
[49] Z. Q. Wang, H. Y. Xu, X. H. Li, H. Yu, Y. C. Liu, X. J. Zhu, Adv. Funct. Mater. 2012, 22, 2759.
[50] C.-C. Hsieh, A. Roy, Y.-F. Chang, D. Shahrjerdi, S. K. Banerjee, Appl. Phys. Lett. 2016, 109, 223501.
[51] Z. Alamgir, K. Beckmann, J. Holt, N. C. Cady, Appl. Phys. Lett. 2017, 111, 063111.
[52] S. Kim, C. Du, P. Sheridan, W. Ma, S. Choi, W. D. Lu, Nanoscale 2015, 15, 2203.
[53] X. Zhu, C. Du, Y. Jeong, W. D. Lu, Nanoscale 2017, 9, 45.
[54] Y.-F. Wang, Y.-C. Lin, I. T. Wang, T.-P. Lin, T.-H. Hou, Sci. Rep. 2015, 5, 10150.
[55] A. A. Bessonov, M. N. Kirikova, D. I. Petukhov, M. Allen, T. Ryhänen, M. J. A. Bailey, Nat. Mater. 2014, 14, 199.
[56] M. Hansen, F. Zahrni, H. Kohlstedt, M. Perniola, R. Ganeshkumar, R. Zhao, presented at IEEE Int. Electron Devices Meeting, San Francisco, CA, December 2014.
[57] S. Yu, B. Gao, Z. Fang, H. Yu, J. Kang, H.-S. P. Wong, Adv. Mater. 2013, 25, 1774.
[58] C. Wang, W. He, Y. Tong, Y. Zhang, K. Huang, L. Song, S. Zhong, R. Ganeshkumar, R. Zhao, Small 2017, 13, 1603435.
[59] J. Yin, F. Zeng, Q. Wan, F. Li, Y. Sun, Y. Hu, J. Liu, C. Li, F. Pan, Adv. Funct. Mater. 2018, 28, 1706927.
[60] S. G. Hu, Y. Liu, Z. Liu, T. P. Chen, J. Wang, Q. Yu, L. J. Deng, Y. Yin, S. Hosaka, Nat. Commun. 2015, 6, 7522.
[61] H. Park, S. Hyun Noh, J. Hye Lee, W. Jun Lee, J. Yun Jaung, S. Geol Lee, T. Hee Han, Sci. Rep. 2015, 5, 14163.
[62] J. Zhang, J. Yan, P. Pageni, Y. Yan, A. Wirth, Y.-P. Chen, Y. Qiao, Q. Wang, A. W. Decho, C. Tang, Sci. Rep. 2015, 5, 11914.
[63] R. Yang, H.-M. Huang, Q.-H. Hong, X.-B. Yin, Z.-H. Tan, T. Shi, Y.-X. Zhou, X.-S. Miao, X.-P. Wang, S.-B. Mi, C.-L. Jia, X. Guo, Adv. Funct. Mater. 2018, 28, 1704455.
[64] A. Serb, J. Bill, A. Khatir, R. Berdan, R. Legenstein, T. Prodromakis, Nat. Commun. 2016, 7, 12611.
