Memory Devices for Flexible and Neuromorphic Device Applications

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Recently, consumer electronics have moved toward data-centric applications due to the development of smart electronic devices. Moreover, electronic devices have become highly portable, wearable, and lightweight. These devices require flexible data storage with high density. Furthermore, with the growing demand for larger memory capacity, faster processing speed, and complex data computation, neuromorphic devices have emerged as the next-generation memory technologies. To meet the needs of next-generation memory devices, memory devices based on emerging materials such as 2D, electrochemical, and perovskite materials are suggested. Herein, the recent progress in emerging materials-based memory devices for flexible and neuromorphic device applications is reviewed. First, the functions and mechanisms of emerging material-based memory devices are described. Second, applications for emerging material-based memory devices are reviewed. Finally, the challenges and prospects for the emerging material-based memory devices are discussed.

1. Introduction

Due to advancements in smart-electronic devices, a huge amount of data is generated, resulting in an increasing demand for high-performance memory devices.\(^1\)–\(^3\) To ensure increased data storage capacities and improved performances, the conventional Si-based memory devices have reduced the device size; this is called downsizing.\(^4\) However, this downsizing has a physical limit because the processes of conventional memory devices are dependent on the lithography limit.\(^5\)–\(^8\) Due to this physical limitation on the downsizing of conventional memory devices, the new-generation memory devices have been developed to meet the demand for memory devices with higher capacities and superior performances.\(^6,9\) Furthermore, these emerging memory devices may have applications that are beyond the scope of conventional memory devices.

The resistive switching mechanism is utilized in emerging memory devices.\(^10,11\) One of the switching mechanisms is based on a conducting bridge that is formed by the redox reactions of metal ions such as silver.\(^12\) Silver ions can migrate across the insulator layer while reducing the silver atoms on the opposite side of the electrode.\(^13\) The silver ions are reduced to the silver molecule; these molecules form the conducting filaments that serve as the electrical path to result in resistive switching.\(^14\) Furthermore, the oxide-based and perovskite-based memory devices utilize the movement of the vacancies for the switching mechanism.\(^15,16\) The migration of oxygen vacancies (or halogen ion vacancies) forms conducting filament in the insulator layer.\(^17\)–\(^19\) These vacancies make a conducting path, and these phenomena lead to resistive switching.\(^20\) In electrochemical memory devices, the redox reactions are utilized as the switching mechanism.\(^21\) In particular, for polymer-based devices, electrochemical redox reactions are utilized for memory devices.\(^22,23\) Because the conductivity of the polymer layers can be affected by the composition of the ions, the redox reactions between ions and an electrolyte layer can be an effective switching mechanism.\(^24\) The redox reactions of the ions in the electrochemical memory devices can induce analog switching, which has advantages for the emulation of the neuromorphic characteristics.\(^25,26\) Also, for the electrochemical devices, polymer-based materials are utilized.\(^27,28\) Because of the versatility of polymer-based materials such as stretchable and flexible properties, electrochemical devices can be utilized in diverse emerging applications.\(^29\)–\(^32\)

Flexible electronics have emerged because of their high portability based on unique physical properties such as flexible and stretchable properties.\(^32\)–\(^34\) In addition, along with the emergence of portable electronic device technology, such as smart glasses, smart watches, and smart bands, the demand for wearable electronic products is growing continuously.\(^35\)–\(^38\) In addition, neuromorphic devices have emerged to overcome the limitations of conventional Si-based devices for the realization of low power consumption computing and big-data analysis.\(^39\)–\(^41\) Based on these features, flexibility and demonstration of neuromorphic functions are important tasks for future electronic devices. Various materials, such as 2D, electrochemical, and perovskite materials, have emerged as next-generation memory devices.\(^42\)–\(^48\) These materials have potential applications in high-performance memory devices as well as in advanced

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memory devices such as flexible and neuromorphic devices.\(^{49,50}\) For practical applications, flexible electronics need to be realized on various nonrigid substrates while ensuring sufficient memory performance.\(^{51}\) Based on these perspectives, various studies have been conducted on flexible memory devices using emerging materials such as 2D, perovskite, and polymer materials.\(^{29,31,32,44,52–55}\)

In addition, neuromorphic computing has emerged as an application of memory devices beyond conventional computing technology.\(^{19,36–58}\) Neuromorphic computing emulates highly complex computation processes of the brain such as synaptic plasticity, backpropagation learning, and nonlinear synaptic weight update.\(^{59}\) The synaptic plasticity indicates the variation in synaptic weights as a function of synaptic activity.\(^{11,60}\) For computation purposes, the synaptic activities of the brain consume only \(\approx 1–10 \text{ fJ} \) per synaptic event.\(^{50}\) Neuromorphic computing emulates these highly efficient computing processes in the brain.\(^{50,61,62}\) Specifically, it imitates the high connectivity and parallel computing in the brain. As a result, it consumes relatively low power and requires fewer processes in memory.\(^{63,64}\)

Recently, complementary metal-oxide-semiconductor (CMOS)-based neuromorphic systems have been launched in the market for artificial intelligence (AI) computing; however, they still have limitations because they are constructed with conventional CMOS hardware.\(^{19,59,60}\) Diverse functional materials have been used in the fabrication of artificial synapses, which are the fundamental building blocks of neural networks.\(^{66–71}\) The critical parameters for neuromorphic computation are the number of memory states, energy consumption, and the operation endurance characteristics.\(^{10,72}\) Furthermore, to evaluate the device performance, the recognition accuracy simulation is required.\(^{12,27,40,73,74}\)

This Review focuses on recent reports of memory devices using emerging materials. As these materials have received attention for possible application in the components of next-generation memory devices, representations of three different materials-based devices will be discussed with an emphasis on materials, operation mechanisms, flexibility, and neuromorphic applications. This Review comprises 1) the introduction of emerging materials for memory devices and their applications, 2) recent research works on 2D material-based devices, electrochemical devices, and perovskite material-based devices for applications in flexible and neuromorphic devices, and 3) a summary of existing challenges in the field of emerging memory technology.

2. Emerging Materials for the Memory Devices

A next-generation memory with superior storage capacity and speed is required to process a massive volume of data.\(^{75}\) Emerging memory devices, such as resistive switching memory, magnetic random-access memory, and phase-change memory have advantages such as a simple device structure and a fast operation speed.\(^{76,77}\) Due to the demand for the diverse applications of memory devices, the next-generation memory devices need to provide versatility in addition to managing a high volume of data.\(^{26,78,79}\) To achieve the aforementioned requirements, memory devices based on various materials such as 2D, electrochemical, and perovskite materials have been suggested.\(^{48,80–83}\) 2D materials have received attention due to their excellent physical properties.\(^{70,82–84}\) Various 2D materials with the electrical properties of conductors, semiconductors, and insulators have been studied. These include graphene, boron nitride (BN), transition metal dichalcogenides (MoS\(_2\) and WS\(_2\)), and black phosphorus (BP).\(^{45,46,85–88}\) They have been widely used in various electronic devices, such as transistors, memories, batteries, and photovoltaics.\(^{89–92}\) Moreover, they are expected to be one of the materials that can replace the conventional Si-based semiconductors due to their lower power consumption and high-efficiency characteristics.

In addition, electrochemical devices have recently emerged for neuromorphic devices.\(^{93}\) These materials have the advantage that they allow ionic flow in the device.\(^{94}\) For example, a p-type semiconductor material, poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) can be utilized for the electrochemical memory devices.\(^{95}\) When voltage is applied to the PEDOT:PSS layer, ionic flow or ionic reaction can be observed in the PEDOT:PSS layer, which causes depletion of holes in the PEDOT: PSS layer.\(^{78,96}\) This leads to a change in the conductivity of the PEDOT:PSS layer.\(^{97–99}\) This change in the carrier density from electrochemical devices takes place over the volume of the electrolyte, which can lead to improved transconductance characteristics.\(^{100}\) In this respect, electrochemical devices have emerged for neuromorphic applications.\(^{21,48,101,102}\)

Furthermore, perovskite-structured materials have been utilized for next-generation memory devices.\(^{100,103–106}\) The structure of the perovskite materials is ABX\(_3\), where A and B are cations; X is the anion.\(^{107}\) The component X, which is generally oxygen or halide ion, can be migrated when an external force is applied to the perovskite materials.\(^{108–110}\) This phenomenon can be utilized in memory devices.\(^{108}\) The migration of vacancies can form the conducting path for the resistive switching operation.\(^{18,44,103}\) Perovskite materials have various structures and compositions, which exhibit versatility in chemical and physical characteristics.\(^{105,109,111,112}\) Therefore, the characteristics of perovskite-based memory devices can be tuned depending on the ions used in the perovskite materials.\(^{105,107,111,113}\) For example, neuromorphic functions can be demonstrated using the migration of ions and defects in the perovskite film under the external electric field.\(^{108,109,114}\) When electric fields are applied to perovskite materials, they exhibit hysteresis in current–voltage curves, which can be applied to neuromorphic devices.\(^{115}\)

3. 2D Material-Based Memory and Applications

3.1. 2D Material-Based Memory Devices

2D materials (graphene, MoS\(_2\), BN, or BP) are the thinnest materials that can provide excellent electronic properties for various applications.\(^{47,116–118}\) Specifically, these materials can offer extremely low power dissipation because they can consist of only one layer of atoms, which represents the ultimate limit of vertical downscaling.\(^{119}\) Therefore, the novel structures and unique physical properties of 2D materials are promising candidates for future electronics.\(^{116,120}\) For example, the MoS\(_2\), one of
the 2D materials was reported as a composition of the memory devices.\textsuperscript{88,121–123} The various switching mechanisms have been suggested for MoS\textsubscript{2} devices such as silver ion migration, vacancy migration, external ion intercalation, and so on.\textsuperscript{112,124–126} MoS\textsubscript{2} can be worked as an insulating layer of the resistive switching memory devices, which are switched by the formation of the conductive filaments. The Ag ions could migrate in the MoS\textsubscript{2} layer and form conducting filaments.\textsuperscript{1127} Because of the unique coordination of the Mo atoms of the MoS\textsubscript{2}, the MoS\textsubscript{2}-based conducting-bridge resistive switching memory devices exhibited low operating voltages.\textsuperscript{128,129} Also, as one of the MoS\textsubscript{2}-based resistive switching memory devices, the atomic lattice changed memory device was reported.\textsuperscript{88,130} MoS\textsubscript{2} has various lattice structures, such as 2H, 3R, and 1T.\textsuperscript{88} Among these, the 1T metallic phase is a metastable structure of MoS\textsubscript{2}.\textsuperscript{131} The 1T-type MoS\textsubscript{2} phase is 10\textsuperscript{2} times more conductive than the 2H phase because of the differences in the energy bandgap.\textsuperscript{132} Based on these theoretical backgrounds, the change phenomena of the lattice formation of the MoS\textsubscript{2} were utilized for the resistive switching memory device (Figure 1a). For the resistive switching devices, the Ag paste was used to deposit the electrodes on the MoS\textsubscript{2} layer.\textsuperscript{88} The structure of the exfoliated 1T-type MoS\textsubscript{2} was investigated using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Figure 1b).\textsuperscript{88} In the atomic resolution images, a clear hexagonal lattice could be observed, which indicated direct evidence of the 1T phase of MoS\textsubscript{2}. The Ag/MoS\textsubscript{2}/Ag device exhibited a hysteresis loop under I–V sweep (Figure 1c). Initially, the device was in the high-resistance state (HRS) and the current was relatively low.\textsuperscript{88} Whereas, at a bias voltage of 66 mV, the current increased abruptly, which indicated the switching behavior of the device. The device exhibited switch-off behavior from low-resistance state (LRS) to HRS at a bias voltage of −98 mV. The device also showed stable switching behavior during 1000 cycles of ON/OFF operation. The switching mechanism of the device is a lattice distortion of the MoS\textsubscript{2} under an electrical field.\textsuperscript{133} For the 1T-type MoS\textsubscript{2} phase, the Mo atoms have octahedral coordination; wherein, the electrons occupy the d\textsubscript{xz}, d\textsubscript{yz}, and p\textsubscript{x} orbitals.\textsuperscript{134} Strong interactions are observed between these orbitals; this leads to the hybridization of these orbitals, which induces the overlapping of the valence and the conduction.\textsuperscript{135}

In addition, a graphene-based memory device was reported.\textsuperscript{45} Graphene has attracted attention from various research areas due to its unique mechanical and electrical properties.\textsuperscript{136,137} As a modified 2D material, polymer-modified graphene oxide (GO) was demonstrated as a memory device. As a hole-transport agent, a triphenylamine-based polyazomethine (TPAPAM) was used as the soluble polymer because of its high mobility, excellent hole injection, and low ionization potential.\textsuperscript{45} The composition of the GO and TPAPAM was synthesized (TPAPAM-GO) to demonstrate the resistive switching memory devices. A TPAPAM-GO-based device exhibited resistive switching memory behaviors. Indium tin oxide (ITO)/TPAPAM-GO/Al, which is a two-terminal structured device, exhibited stable switching.

![Figure 1](image-url) Figure 1. Memory characteristics of the 2D material-based electronic devices. a) Schematic structure of Ag/MoS\textsubscript{2}/Ag resistive switching memory device. b) HAADF-STEM image of MoS\textsubscript{2}. The blue dots show the hexagonal lattice arrangement of the Mo atoms. c) I–V characteristics of Ag/MoS\textsubscript{2}/Ag resistive switching memory device. d) Resistive switching characteristics of an ITO/TPAPAM-GO/Al device. e) Schematic of the light modulation of the BP@PS resistive switching memory. The device characteristics could be modulated by the wavelengths of the light. f) I–V curves of the BP@PS resistive switching characteristics modulated by different wavelengths. a–c Reproduced with permission.\textsuperscript{48} Copyright 2016, American Chemical Society. d) Reproduced with permission.\textsuperscript{[45]} Copyright 2010, John Wiley & Sons. e,f) Reproduced with permission.\textsuperscript{[46]} Copyright 2020, American Chemical Society.
characteristics, and showed an ON/OFF current ratio of $10^4$ at $-1\text{ V}$. [Figure 1d]. At the switching voltages, electrons were transported into the graphene monolayer from the TPAPAM. Because of these transmitted electrons, the reduced graphene oxide (rGO) was oxidized, which exhibits a relatively higher resistance than rGO.\(^{[138]}\) It was hence observed that these redox reactions led to resistive switching phenomena.

Another 2D material, BP, has a broad light absorption range.\(^{[140]}\) A transparent resistive switching memory device based on the BP was reported. The two-terminal structured device, ITO/BP@PS/ITO, was composed of ITO electrodes and BP nanosheets coated with polystyrene (BP@PS) (Figure 1e). The resistive switching characteristics were observed in this BP@PS-based device. Specifically, the device was abruptly switched from HRS to LRS at $-0.5\text{ V}$. In contrast, at a voltage of $2\text{ V}$, the device switched back to its initial resistance state, i.e., from HRS to LRS. During the device fabrication process, BP could be partially oxidized by oxygen in the air. Because of these oxygen atoms in the BP layer, a conducting path was formed in the device during the switching process.\(^{[138]}\) The resistive switching characteristics of the BP@PS-based memory device could also be induced by photonic stimuli due to trapping of the photogenerated electrons at trapping sites in the BP layer.\(^{[46]}\) Depending on the wavelengths of the light inputs, the switching voltages were modulated. The average switching voltages were reduced when shorter wavelength light inputs were applied (Figure 1f). Under UV light, the device exhibited lower power consumption than in the case of light inputs with longer wavelengths. Moreover, the device performance was not degraded during UV light illumination and showed stable switching characteristics. The increment of Schottky barrier height due to the trapping of photogenerated electrons led to the modification of the resistive switching characteristics of the BP-based memory device.\(^{[46]}\) These results provide novel approaches to enhance the performance of memory devices using 2D materials and their unique properties.

### 3.2. Applications of the 2D Material-Based Memory Devices

#### 3.2.1. Flexible Applications

A MoS$_2$–polyvinylpyrrolidone (MoS$_2$–PVP) nanocomposite was reported as a component of a flexible memory device.\(^{[33]}\) Due to poor wetting properties and 2D plane structure of MoS$_2$, PVP was used to form a film.\(^{[139]–141]}\) The flexible memory device was demonstrated using MoS$_2$–PVP and rGO. At the initial state, the MoS$_2$–PVP was stacked (Figure 2a). To demonstrate the nanosheet-structured MoS$_2$–PVP, the MoS$_2$ powder was sonicated in ethanol in the presence of PVP to synthesize the MoS$_2$–PVP nanocomposites, which served as the insulator layer of the memory device (Figure 2b).\(^{[142]}\) The MoS$_2$–PVP-based device exhibited memory behavior (Figure 2c).\(^{[143]}\) The switching operation of the device was induced by the charge trapping and detrapping behavior of MoS$_2$ in the PVP.\(^{[144]}\) The device had large electron and hole injection barriers under a positive voltage, therefore charge transfer between MoS$_2$–PVP and rGO did not occur at a voltage lower than the switching voltage (4 V). However, when a voltage higher than the switching voltage was applied to the device, charge transfer occurred and electrons were trapped in the MoS$_2$, which resulted in the LRS. During the positive voltage sweep, it exhibited a progressive current increment with an increasing voltage. At the switching voltage, the current of the device increased abruptly, which indicated the switching from HRS to LRS. The charge trapping and detrapping behavior of MoS$_2$ in the PVP led to this switching behavior of the device.\(^{[145]}\) Moreover, when a negative voltage was applied, the device switched back to the HRS, which represented the transition from LRS to HRS. Because of the flexibility of the components, MoS$_2$–PVP and rGO, the device exhibited flexible characteristics.\(^{[33]}\) This device exhibited stable switching characteristics under the bent states.

In addition, 2D materials can be utilized for printed electronics.\(^{[34,144,146,147]}\) A fully inkjet-printed field-effect transistors (FETs) using 2D materials such as graphene and hexagonal-BN have been used for flexible memory applications (Figure 2d).\(^{[146]}\) The graphene transistor channel was printed on a polyethylene terephthalate (PET) substrate using graphene ink. Subsequently, silver source/drain electrodes and h-BN gate dielectric were printed using silver ink and h-BN ink, respectively.\(^{[146]}\) The device was also fabricated on a polyester satin fabric (Figure 2e), which was a highly durable and widely used material for clothes.\(^{[149]}\) The mobility of this device was two to three times higher than that of the organic FETs on e-textile fibers.\(^{[146,148]}\) For practical applications, textiles must endure tensile and washing environments.\(^{[146]}\) To verify the device performance, the device characteristics were measured during the bending operations and after washing. The mobility of the devices did not change significantly, indicating that the devices were stable during the bending operations (Figure 2f). In addition, after washing, the device did not show significant degradation (Figure 2g). Moreover, the suggested 2D material-based devices have the potential to enable fully inkjet-printed electronic circuits such as complementary inverters and logic gates.\(^{[149]}\)

#### 3.2.2. Neuromorphic Applications

An artificial synapse using twisted bilayer graphene was reported to demonstrate neuromorphic characteristics. The device was composed of a bottom Si gate, twisted bilayer graphene, Al oxide layer, the source, drain, and the top electrodes (Figure 3a).\(^{[150]}\) AlO$_x$ dielectric layer was deposited by the oxidation of the Al layer and the twisted bilayer graphene layer was deposited on the Si substrate. The twisted bilayer graphene layers had two independent layers of the graphene which were operated separately by the electric fields from the top and bottom gates. Twisted bilayer graphene was used as a channel material to achieve multilevel conductance modulation characteristics of an artificial synapse.\(^{[151,152]}\) The presynaptic inputs were provided in the form of applied voltages to the top gate electrodes, which increased the amount of induced carrier and caused a rise in drain current. The applied voltages led to the change of synaptic plasticity, which was induced by the charge trapping of the carriers in the graphene layer. Furthermore, the postsynaptic current (PSC) characteristics under consecutive voltage pulses were demonstrated (Figure 3b). Because graphene exhibited the ambipolar conductance property, the majority carriers, i.e., either electrons or holes, were switched depending on the applied electric...
Based on these properties, the excitatory and inhibitory synaptic characteristics could be emulated depending on the position of the gate electrodes and polarity of applied voltages with the twisted bilayer graphene. Under a positive bottom gate voltage (2 V, 10 ms), the device exhibited inhibitory postsynaptic current (IPSC) characteristics. The amplitudes of the PSC decreased when the positive pulses were applied to the top gate. Oppositely, when negative pulses (−2 V, 10 ms) were applied to the top gate, the device exhibited excitatory postsynaptic current (EPSC) characteristics. The peak amplitudes of the PSC increased as pulses applied. This behavior could be reversed using a negative bottom-gate voltage. In addition, the spike-timing-dependent plasticity (STDP) functions were demonstrated using the device (Figure 3c). Under a positive bottom gate voltage, the device exhibited inhibitory synaptic characteristics. Whereas, under a negative bottom gate voltage, the device exhibited excitatory synaptic characteristics.

Layered BP, an emerging 2D material, has attracted attention for electronic devices owing to its high mobility, moderate bandgap, and anisotropic characteristics. At the surface of the multilayer BP, the phosphorus oxide is formed in the air. Because of the phosphorus oxide at the BP layers, the multilayer BP has the heterostructure between BP and phosphorus oxide. This heterostructure of the multilayer BP has advantages for emulating the synaptic functions as the conductance of the device can be controlled by the external electrical inputs. Based on these perspectives, phosphorus oxide/BP heterostructure was utilized for neuromorphic applications (Figure 3d). BP flakes were exfoliated onto a SiO$_2$/Si substrate. To form the electrical contact between the BP and electrodes, Au/Cr was deposited as the source and drain electrodes. The current of the BP channel decreased sharply when a positive pulse was applied at the gate due to the injection of electrons from the channel into the oxide layer. Because the BP showed different electrical characteristics depending on the orientation of the crystal, the device exhibited significantly different characteristics depending on the direction of the electrodes. Specifically, the carrier mobility of the BP varied along the $x$- and $y$-directions when electrons were trapped in the oxide. Based on these features, the BP-based device was adopted for anisotropic synaptic connections (Figure 3e). In a brain, multiple presynaptic neurons are connected to a postsynaptic neuron through the synapses with a heterogeneous connection. The strength of the signals of each presynaptic neuron could be different from that of other presynaptic neurons. To demonstrate these anisotropic synaptic connections, the electrodes were deposited in eight directions to observe the effect of the $x$- and $y$-directions. The artificial synapse based on BP exhibited direction-dependent characteristics. In particular, the strength of each connection of the device varied due to the different orientations of the BP crystal (Figure 3f). The four synaptic devices, each consisting of an artificial anisotropic component, were measured simultaneously to study their PSC characteristics. Depending on the direction of the artificial anisotropic component, all of these four synaptic devices could be operated simultaneously using a pulse train.
MoS\textsubscript{2} was also utilized to demonstrate neuromorphic functions. The two electrodes were contacted with the MoS\textsubscript{2} monolayer to demonstrate the artificial synapse, which was operated by Joule heating (Figure 3g).\cite{165} The Joule heating of the MoS\textsubscript{2} led to the conductance change using only 10 fJ of energy for heating.\cite{165} This extremely low power consumption characteristic was originated from the metal–insulator transition, which controlled the carrier density in MoS\textsubscript{2}. The electrical characteristics of the device were depending on the condition of the applied pulses such as interval, width, frequency, and number of the pulses. These characteristics could induce the neuromorphic functions.\cite{166} The device emulated synaptic facilitation characteristics of the biological synapse.\cite{167} When voltage pulses were applied to the device, the conductance of the device gradually increased. The hysteresis in the $I$–$V$ curves was observed under repeated $I$–$V$ measurement cycles (Figure 3h). Because of the Joule heating effect in MoS\textsubscript{2}, the conductance of the device increased during the $I$–$V$ sweep. When the stimuli were removed, the conductance of the device decayed back to its initial value, which was similar to the short-term plasticity (STP) characteristics of a biological synapse. The MoS\textsubscript{2}-based artificial synapse device exhibited paired-pulse facilitation (PPF) characteristics. When the voltage pulses with a short interval were applied to the MoS\textsubscript{2} channel, the responses of the device increased during the second pulse because of the residual temperature of the MoS\textsubscript{2}.\cite{167,168} Based on these features, the device exhibited a higher response current as the time interval of the voltage pulses decreased (Figure 3i). In addition, the device exhibited inhibitory characteristics due to the heavily n-doped MoS\textsubscript{2} channel. Furthermore, this device was adopted to realize sound localization.

In summary, the 2D material-based memory devices exhibited lower energy consumption and stable switching characteristics because of the superior physical and electrical properties of 2D materials.\cite{122,146,147,169–172} However, the manufacturing of memory devices based on 2D materials has challenges such

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Figure 3. Neuromorphic applications of the 2D material-based memory devices. a) Schematic illustration of the graphene-based neuromorphic device. b) Potentiation/depression characteristics and c) STDP characteristics of the graphene-based device. d) Schematic illustration of the multigate neuromorphic device using BP. e) The testing scheme of a multisynapse network. f) Simultaneous change of positive and negative weight in a multisynapse network. g) Schematic illustrations of the neuromorphic device based on the monolayer MoS\textsubscript{2}. h) Conductance facilitation driven by Joule heating with multiple voltage sweeps. i) The facilitation and depression behaviors of the device. a–c) Reproduced with permission.\cite{150} Copyright 2015, American Chemical Society. d–f) Reproduced with permission.\cite{135} Copyright 2016, John Wiley & Sons. g–i) Reproduced with permission.\cite{165} Copyright 2018, American Chemical Society.
as high manufacturing cost and complicated processes. Nevertheless, 2D materials have been utilized in memory devices because of their unique electrical and physical characteristics such as bidirectional conductivity, optical response characteristics, and flexibility. The development of new processes for large-area deposition such as bottom-up processes is required to overcome these challenges.

4. Electrochemical Memory Devices and Applications

4.1. Electrochemical Memory Devices

In electrochemical memory devices, the accumulation of charges or ions on the interface between the electrolyte and channel layer modified the channel conductance. A redox-based electrochemical device was demonstrated using a composite of BP and triphenylamine. The BP was passivated and electrochemically activated by a covalent bonding modification process using diazonium tetrafluoroborate of triphenylamine (BPNSs-TPA). In the memory devices, BPNSs-TPA and ethyl viologen diperchlorate (EV(ClO$_4$)$_2$) were utilized as the switching material (Figure 4a). The device had a two-terminal structure, with ITO and Pt/Ti as bottom and top electrodes, respectively. The switching behavior of the BPNSs-TPA could be demonstrated by the reversible redox reaction (i.e., exchange of ClO$_4^-$ ions) between the EV(ClO$_4$)$_2$ and TPA (Figure 4b). Under the negative electric field, the device switched from HRS to LRS. The lone-pair electrons from the N atoms in BPNSs–TPA were removed under the influence of a negative electric field, which indicated the oxidation of the BPNSs–TPA (Figure 4c). When the negative electric field was applied to the working electrode, EV(ClO$_4$)$_2$ was reduced at the counter electrode and the ClO$_4^-$ ions were migrated to the working electrode. Both processes were reversible reactions. When a positive electric field was applied, BPNSs–TPA was reduced and ClO$_4^-$ ions moved back into the EV(ClO$_4$)$_2$. Based on these features, the device exhibited switching characteristics.

4.2. Applications of the Electrochemical Memory Devices

4.2.1. Flexible Applications

Electrochemical devices have advantages for flexible applications. Flexible electrochemical memory devices were reported using synthesized aromatic polyimides with starburst triarylamine (Figure 4d). Polyimide or polyamide had advantages for the ion exchange reactions containing electron donors. These materials exhibited chemical stability, mechanical strength, and high transconductance. The starburst triarylamine units have low oxidation potential. Therefore, the composite of the starburst triarylamine and polyimide materials was expected to be electrochemically stable (Figure 4e). The flexible memory devices thus exhibited stable switching characteristics under various bending conditions. Specifically, during the bending operation, the device did not show any physical degradation (Figure 4f). Moreover, the device presented reliable and stable switching characteristics under mechanically stressed conditions. This device has the potential for electrochemical flexible memory devices.

Figure 4. Electrochemical memory devices. a) Schematic illustration of the device. b) The chemical structures of active materials. c) Resistive switching behaviors of the device. Schematic illustrations of the d) memory layers and e) device structure. f) Resistive switching behavior of the device. a–c) Reproduced with permission.[85] Copyright 2013, Royal Society of Chemistry. d–f) Reproduced with permission.[52] Copyright 2013, John Wiley & Sons.
4.2.2. Neuromorphic Applications

Electrochemical devices have attracted attention as promising candidates for neuromorphic memory devices due to their linear synaptic plasticity updates, symmetrical conductance responses, low power consumption, and multilevel characteristic that are appropriate for neuromorphic applications.\cite{176} An electrochemical synaptic device based on graphene was reported (Figure 5a).\cite{21} For neuromorphic applications, the devices are required to have a multilevel, reversible switching process, good endurance, long retention, fast switching speed, and low operating power consumption characteristics. To achieve these requirements, graphene was utilized for neuromorphic applications.\cite{10,40,77,78} As graphene could absorb/desorb metal ions, it was utilized for postsynaptic neurons.\cite{177} The conductance of the graphene represented the synaptic weight, and it could be modulated by the electrical signals. The graphene-based electrochemical device could achieve reversible and precise tuning of the channel conductance by intercalation of the Li ions. When an external current was applied to the device, the Li ions were intercalated into the graphene, thus resulting in a decreased channel conductance.\cite{21,82,177,178} Based on these features, the device exhibited synaptic potentiation and depression (Figure 5b). Applying the intercalation and deintercalation pulses to the device, it exhibited long-term potentiation and depression characteristics (over 250 distinct states).\cite{179}

In addition, neuromorphic applications of electrochemical devices based on Li-intercalation mechanisms and solid electrolytes were reported.\cite{176} The suggested device called a “Li-ion synaptic transistor for analog computation (LISTA)” is a nonvolatile redox-based transistor. The resistance of the device could be precisely modulated using the intercalation phenomenon of Li ions. The device used Li$_{1-x}$CoO$_2$ and Li ions for the neuromorphic device because the activation energy of Li diffusion was low in Li$_{1-x}$CoO$_2$ and Li$_{1-x}$CoO$_2$ exhibited stable and reliable redox reactions with the Li ions.\cite{180–182} For the neuromorphic device, Pt was used as the source and drain electrodes. Lithium phosphorous oxynitride (LiPON) was used as the electrolyte layer to

![Figure 5. Neuromorphic applications of the electrochemical memory devices. a) Schematic illustration of the operating mechanisms of the Li-intercalated graphene device. b) Repetition of the potentiation and depression operations of the device. c) The potentiation and depression operation endurance test of the LISTA device. d) Schematic illustration of the array of the LISTA devices for the neuromorphic simulation. e) Modified National Institute of Standards and Technology database (MNIST) simulation results of the LISTA device. a,b) Reproduced with permission.\cite{21} Copyright 2018, John Wiley & Sons. c–e) Reproduced with permission.\cite{176} Copyright 2016, John Wiley & Sons.](image-url)
separate the channel from the Si gate electrode.\textsuperscript{183,184} When voltages were applied to the gate electrode, the Li content in the channel was regulated; this controlled the channel conductivity. The multilevel states were demonstrated by applying voltage pulses (Figure 5c). During the writing process, the device exhibited stable switching characteristics. Furthermore, a neural network was demonstrated with the suggested device. The device was tested with CrossSim, which consisted of a three-layer network.\textsuperscript{176} Two matrices of the devices were carried out on a simulated crossbar (Figure 5d). The device exhibited 90% of the recognition accuracy within the second epoch of the simulation (Figure 5e).

Electrochemical memory devices are specialized for precise control of the resistive states.\textsuperscript{89} These properties have advantages for the demonstration of neuromorphic functions.\textsuperscript{27,185–187} Furthermore, electrochemical memory devices can be easily utilized for flexible devices because most of the devices consist of polymer materials.\textsuperscript{49} The electrochemical memory devices can be demonstrated as flexible neuromorphic memory devices, which are appropriate for future electronics. They can be utilized as highly efficient and portable electronics. Based on these perspectives, electrochemical devices have emerged as materials for next-generation memory devices.\textsuperscript{27,51,89} The high-level integration of the electrochemical devices remains for practical application.

5. Perovskite Materials-Based Memory and Applications

5.1. Memory Devices Based on the Perovskite-Structured Materials

Perovskite materials have a 3D octahedral crystal structure.\textsuperscript{188} Based on this crystal structure, perovskite materials have structural flexibility, which leads to versatile electrical behaviors.\textsuperscript{25} Charge trapping, ion migration, and defect migration phenomena of the perovskite materials result in hysteresis curves in the $I$–$V$ sweep, which is associated with switching behaviors.\textsuperscript{189,190} Under the external electric field, the defects, vacancies, interstitials, and antisites can migrate within the perovskite materials, which affects their electrical characteristics.\textsuperscript{188,191} In perovskite-based memory devices, ion migration plays a vital role in switching behaviors.\textsuperscript{192} These charge trapping abilities, ion migration properties, and low-temperature processability of the perovskite materials indicate the potential to be applied for the memory devices.\textsuperscript{17,193}

The electrical devices using perovskite materials exhibited hysteresis in the $I$–$V$ curves.\textsuperscript{189} Based on the hysteresis of perovskite materials, resistive switching behaviors were reported for perovskite films sandwiched between two electrodes.\textsuperscript{191} For example, resistive switching behavior was observed in MAPbI$_3$\textsuperscript{190,194} In this device, the point defects, I$^-$ and MA$^+$, were migrated in the perovskite materials under the influence of an electric field and caused the resistive switching phenomenon.\textsuperscript{193} This is because the shallow defects, which are formed by ion migration, lead to a decreased electric resistance of the perovskite materials.\textsuperscript{8,193,196} Based on this background, resistive switching memory devices with MAPbI$_3$ were reported.\textsuperscript{192} A two-terminal structured device (metal/MAPbI$_3$/Au) was demonstrated for resistive switching characteristics (Figure 6a).\textsuperscript{192} The formation or annihilation of the conduction channel was realized by the iodine vacancies under the influence of the electrical field. In the initial state, the device exhibited the HRS. With the application of positive voltages, the device switched to the LRS at 3 V (Figure 6b). When negative gate voltages were applied, the resistance of the device was switched back to HRS. The reliability of the device was confirmed by consecutive switching from LRS to HRS over 1000 times (Figure 6c). In addition, the characteristics of perovskite materials can be tuned by the components of the perovskite materials. Based on a layered (PEA)$_3$PbBr$_2$ perovskite single crystal, a resistive switching memory device was reported to exhibit an extremely low operating current.\textsuperscript{114} In the (PEA)$_3$PbBr$_2$, the conducting channel was formed by the migration of the Br ions when subjected to an electric field. After the formation of the conductive filament based on ion vacancies, the concentration of the Br ions was higher at the interface between (PEA)$_3$PbBr$_2$ and Au, which indicated the migration of the Br ions. To confirm the formation of the conducting filament, a detailed analysis was conducted using a transmission-electron microscope (TEM) imaging (Figure 6d). In the cross-sectional image, when positive voltages were applied to the Au electrode, the diameter of the filament was observed to be wider at the graphene side. This implied that the migrated ions were negatively charged, which were Br ions. When applying higher stress to the device, an abrupt change in current was observed from 0.1 (HRS) to 10 pA (LRS) (Figure 6e). The abrupt increment of the current indicated that conductive filaments were formed in the perovskite materials. The current at HRS, 0.1 pA, could be considered suitable for low power consumption applications (Figure 6f). Furthermore, the device exhibited an extremely low off-current because the charge transport in the out-of-plane direction of the 2D perovskite films was inhibited.

5.2. Applications of the Perovskite Material-Based Memory Devices

5.2.1. Flexible Applications

Perovskite materials are emerging components of flexible memory devices because of their mechanical flexibility, simple fabrication process, and low cost.\textsuperscript{18,25,30,110,115,197} The flexible memory device based on the perovskite materials was demonstrated on the flexible substrates, PET. The crystallized perovskite films were utilized for the resistive switching layer. A two-terminal structured device, Al/CsPbBr$_3$/PEDOT:PSS/ITO/PET, exhibited reproducible and reliable characteristics during switching operations.\textsuperscript{50} During the direct current (DC) voltage sweep, the memory device showed bipolar resistive switching characteristics. By applying negative voltages, the device was switched from the HRS to the LRS. In addition, the device exhibited self-compliance characteristics because of the parasitic resistance of the PEDOT:PSS and ITO layers in the device. Moreover, the device exhibited flexible memory characteristics.\textsuperscript{109} To verify the mechanical endurance and flexibility, the device was tested under bending operations (Figure 7a,b). It was observed that the device exhibited stable resistive switching characteristics even in the
bending states (Figure 7c). Specifically, during bending, the device exhibited stable resistive switching characteristics when the bending angle was 0°, 120°, 180°, and 360°. In addition, a flexible perovskite-based memory device with transparent characteristics has also been demonstrated. Transparent and flexible ITO/Ag/BaTiCoO (BTCO)/Ag-doped ITO (Ag-ITO) heterostructure films were deposited on 2D fluorophlogopite mica[110,198]. The device showed resistive switching characteristics at a 2.2 mm bending radius. To confirm its flexibility, resistive switching characteristics were measured during the bending operation (Figure 7d). The device did not show any significant differences in its switching characteristics at flat and bent states.[198] The two-terminal structured device, ITO/Ag/BTCO/Ag-ITO/mica-based resistive switching memory, exhibited reversible unipolar resistive switching characteristics (Figure 7e). By applying a positive voltage, the device was switched from HRS to LRS at 0.5 V, whereas in the reset process, LRS to HRS, the device was switched at 1.2 V. The switching characteristics of the device were not changed significantly during the bending processes. Moreover, the device exhibited stable and reliable HRS and LRS characteristics during the bending cycles (Figure 7f).

5.2.2. Neuromorphic Applications

The ion migration properties of perovskite materials can be utilized in synapse devices as well as resistive switching memory devices. Due to their inherent low conductivity, perovskite
materials have emerged as materials for neuromorphic devices with low power consumption. Based on these perspectives, an artificial synapse using a Br-based organo-metal halide perovskite (OHP, CH$_3$NH$_3$PbBr$_3$) was reported for neuromorphic applications. The perovskite-based artificial synapse emulated synaptic characteristics such as EPSC, PPF, STP, long-term plasticity (LTP), and STDP. The artificial synapse was fabricated using the substrate/buffer-capped conducting polymer (BCCP) electrode, MAPbBr$_3$, and Al top electrodes (Figure 8a,b). The BCCP thin film and the bottom electrode represented the postsynaptic neuron, which received the transmitted electrical information from the presynaptic neuron (i.e., Al top electrode). The perovskite layer MAPbBr$_3$ represented the synapse of the neural network, which transmitted the information from the presynaptic neuron to the postsynaptic neuron. The conductance of the OHP film was modified by presynaptic pulses. By applying the presynaptic inputs to the top electrode, the migration of the ions could be induced, which led to the synaptic weight change of the device. The main operation mechanism of this device was the formation of conductive paths caused by the ion migration within the perovskite material. The electrical pulses drove the migration of ions in perovskite materials, and it could form conductive filaments in the perovskite layer, which led to the observed conductivity variations. Under low amplitude of pulses, the ions in the perovskite layer could migrate a short distance and returned to their initial position. In this case, the conductance of the device increased sharply and recovered to the initial state, which represented STP. In contrast, with strong stimulation, the ions in perovskite materials could be moved to a sufficiently long distance for them to be trapped at the interface between OHP and BCCP. After strong stimulation, some of the ions could not be returned to their equilibrium position. Consequently, the conductance of the device was reduced in the long term, which was represented by LTP. In addition, the time of the applied stimuli was one of the variables of synaptic plasticity of the device (Figure 8c). The amplitude of the EPSC depended on the time interval of the applied stimuli.

In addition, an all-inorganic perovskite, CsPbBr$_3$, was utilized for neuromorphic applications. To demonstrate the artificial synapse, quantum dots of CsPbBr$_3$ (CsPbBr$_3$ QD) were used as the switching material. The synaptic characteristics of the device were induced by the heterostructure between the semiconductor and the CsPbBr$_3$ QDs. This device emulated the synaptic functions, including STP, LTP, and spike-rate-dependent plasticity (SRDP) characteristics. Furthermore, this device emulated synaptic functions using optical stimuli. A three-terminal photonic synapse based on CsPbBr$_3$ QDs was demonstrated using Si/SiO$_2$/CsPbBr$_3$ QDs/poly(methyl methacrylate) (PMMA)/pentacene/Au source-drain electrodes (Figure 8d). CsPbBr$_3$ QDs were used as the floating gate of the device, and pentacene was used as the channel of the device. The device could be programmed and achieved multilevel memory characteristics using light inputs (Figure 8e).
potentiation/depression characteristics using optical programming and electrical erasing operations (Figure 8f).

Perovskite materials can be applied as 2D materials, electrolytes, and resistive switching materials. Because of this versatility, they have emerged as components of next-generation memory devices. However, these materials are easily degraded by humidity and heat. Furthermore, some perovskite materials contain toxic elements such as Pb. These issues should be solved for their practical applications. Development of packaging, Pb-free perovskites, and environment-resistant perovskites could be solutions for the future perovskite-based memory devices.

Comparison of device performance of the emerging material-based devices is shown in Table 1.

6. Conclusion

In this review, promising emerging materials that can be used to realize emerging memory devices and applications are discussed. The current status of emerging memory technologies, along with existing challenges, is reported. Moreover, emerging materials for memory devices and important memory applications are provided. Specifically, the fundamental knowledge of emerging materials for the next-generation memory device, device applications, and recent research on memories are highlighted. 2D, electrochemical, and perovskite materials are considered promising next-generation materials for nonvolatile memory devices due to their cost-effective and extraordinary memory properties. In particular, the characteristics of emerging

Table 1. Comparison of device performance of the emerging material-based devices.

|                            | Material   | On/off ratio | Operating source | Endurance | Retention | Flexibility | STDP | Ref.        |
|-----------------------------|------------|--------------|-------------------|-----------|-----------|-------------|------|------------|
| CMOS-based                  | Si         | ≈10          | 0.55–1 V          | N/A       | N/A       | N/A         | O    | [200]      |
| 2D materials                | MoS₂       | ≈1.7         | 5 V               | N/A       | N/A       | N/A         | N/A  | [165]      |
|                            | Graphene   | ≈1.2         | 2 V               | N/A       | N/A       | N/A         | O    | [150]      |
|                            | BP         | ≈1.2         | 20 V              | N/A       | N/A       | N/A         | O    | [155]      |
| Electrochemical materials   | Graphene:LFP| 12           | 50 pA             | >7        | >4 ms     | O           | O    | [21]       |
|                            | LiPON: Li₄CoO₂ | ≈1.6       | 100 mV            | >30       | 7 months  | N/A         | O    | [176]      |
| Perovskite materials        | MAPbBr₂     | >10⁷         | 0.1 V             | N/A       | <20 s     | N/A         | N/A  | [109]      |
|                            | CsPbBr₁     | ≈4           | 30 V              | >1000     | >10 year  | N/A         | O    | [108]      |
material-based memory devices are provided regarding the performance of the device, such as the ON/OFF ratio, endurance, retention capability, flexibility, and neuromorphic performance. Despite significant progress in materials research on memory technology in recent years, there remain some challenges, such as high-level integration, long-term reliability, CMOS compatibility, and electrical uniformity. To overcome the challenges for future memory devices, the reliability and processability of the emerging materials for memory devices need to be enhanced. Nevertheless, the emerging material-based memory devices have a great potential for the application such as neuromorphic devices, biofriendly devices, and wearable devices. Because research on emerging material-based memory devices is accelerated and rapidly increases, great progress in memory technology will be viable in the near future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D materials, electrochemical devices, flexible electronics, memory devices, neuromorphic applications, perovskite materials

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[1] D. Lazer, R. Kennedy, G. King, A. Vespignani, Science 2014, 343, 1203.
[2] Q. Zhang, L. T. Yang, Z. Chen, P. Li, Inf. Fusion 2018, 42, 146.
[3] A. Gandomi, M. Haider, Int. J. Inf. Manage. 2015, 35, 137.
[4] I. I. Markov, Nature 2014, 512, 147.
[5] T. Schenk, M. Pešić, S. Slesazeck, U. Schroeder, T. Mikolajic, Rep. Prog. Phys. 2020, 83, 086501.
[6] S. Yu, P.-Y. Chen, IEEE Solid-State Circuits Mag. 2016, 8, 43.
[7] S. Lloyd, Nature 2000, 406, 1047.
[8] J. J. Yang, D. B. Strukov, D. R. Stewart, Nat. Nanotechnol. 2013, 8, 13.
[9] H. S. P. Wong, H. Y. Lee, S. Yu, Y. S. Chen, Y. Wu, P. P. Chen, B. Lee, F. T. Chen, M. J. Tsai, Proc. IEEE 2012, 100, 1951.
[10] Z. R. Wang, H. Q. Wu, G. W. Burr, C. S. Hwang, K. L. Wang, Q. F. Xia, J. J. Yang, Nat. Rev. Mater. 2020, 5, 173.
[11] M. R. Zhao, B. Gao, J. S. Tang, H. Qian, H. Q. Wu, Appl. Phys. Rev. 2020, 7, 011301.
[12] S. Choi, S. H. Tan, Z. Li, Y. Kim, C. Choi, P. Y. Chen, H. Yeon, S. Yu, J. Kim, Nat. Mater. 2018, 17, 335.
[13] Y. Yang, P. Gao, S. Gaba, T. Chang, X. Pan, W. Lu, Nat. Commun. 2012, 3, 732.
[119] Y. Yoon, K. Ganapathi, S. Salahuddin, *Nano Lett.* 2011, 11, 3768.
[120] A. K. Geim, *Science* 2009, 324, 1530.
[121] G. Gao, B. Wan, X. Liu, Q. Sun, X. Yang, L. Wang, C. Pan, Z. L. Wang, *Adv. Mater.* 2018, 30, 1705088.
[122] S. Wang, C. Chen, Z. Yu, Y. He, X. Chen, Q. Wan, Y. Shi, D. W. Zhang, H. Zhou, X. Wang, P. Zhou, *Adv. Mater.* 2019, 31, 1806227.
[123] F. A. McCuire, Y.-C. Lin, K. Price, G. B. Rayner, S. Khandelwal, S. Salahuddin, A. D. Franklin, *Nano Lett.* 2017, 17, 4801.
[124] S. Yin, Z. Luo, Q. Li, C. Xiong, Y. Liu, R. Singh, F. Zeng, Y. Zhong, X. Zhang, *Phys. Status Solidi A* 2019, 216, 1900104.
[125] X. Zhu, D. Li, X. Liang, W. D. Lu, *Nat. Mater.* 2019, 18, 141.
[126] D. Li, B. Wu, X. Zhu, J. Wang, B. Ruy, W. D. Lu, W. Lu, X. Liang, *ACS Nano* 2018, 12, 9240.
[127] R. Ge, X. Wu, M. Kim, J. Shi, S. Sonde, L. Tao, Y. Zhang, J. C. Lee, D. Akinwande, *Nano Lett.* 2018, 18, 434.
[128] X. Zhao, Z. Fan, H. Xu, Z. Wang, J. Xu, J. Ma, Y. Liu, J. Mater. Chem. C 2018, 6, 7195.
[129] R. Xu, H. Jang, M.-H. Lee, D. Amanov, Y. Cho, H. Kim, S. Park, H.-J. Shin, D. Ham, *Nano Lett.* 2019, 19, 2411.
[130] J. Su, L. Feng, W. Zeng, Z. Liu, *Nanoscale* 2017, 9, 7429.
[131] M. Acerce, D. Voiry, M. Chhowalla, *Nat. Nanotechnol.* 2015, 10, 313.
[132] R. Kapper, D. Voiry, S. E. Yalcin, B. Branch, G. Gupta, A. D. Mohite, M. Chhowalla, *Nat. Mater.* 2014, 13, 1128.
[133] S. Shi, Z. Sun, Y. H. Hu, *J. Mater. Chem. A* 2018, 6, 23932.
[134] T. Heine, *Acc. Chem. Res.* 2015, 48, 65.
[135] Z. Lei, J. Zhan, L. Tang, Y. Zhang, Y. Wang, *Adv. Energy Mater.* 2018, 8, 1703482.
[136] X. Zhao, J. Ma, X. Xiao, Q. Liu, L. Shao, D. Chen, S. Liu, J. Niu, X. Zhang, Y. Wang, R. Cao, W. Wang, Z. Di, H. Lv, S. Long, M. Liu, *Adv. Mater.* 2018, 30, 1705193.
[137] Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, R. S. Ruoff, *Adv. Mater.* 2010, 22, 3906.
[138] C. X. Hao, F. S. Wen, J. Y. Xiang, S. J. Yuan, B. C. Yang, L. Li, W. H. Wang, Z. M. Zeng, L. M. Wang, Z. Y. Liu, J. T. Tian, *Adv. Funct. Mater.* 2016, 26, 2016.
[139] A. B. Bourlinos, V. Georgakilas, R. Zboril, T. A. Steiger, A. K. Stobbs, C. Trapani, *Solid State Commun.* 2009, 149, 2172.
[140] A. S. Wajid, S. Das, F. Irin, H. S. T. Ahmed, J. L. Shellburne, D. Parviz, R. J. Fullerton, A. F. Jankowski, R. C. Hedden, M. J. Green, *Carbon* 2012, 50, 526.
[141] A. M. Koo, H. T. Ham, M. H. Choi, S. O. Kim, I. J. Chung, *Polymer* 2003, 44, 681.
[142] K.-C. Zhou, N.-N. Mao, H.-X. Wang, Y. Peng, H.-L. Zhang, *Angew. Chem., Int. Ed.* 2011, 50, 10839.
[143] C. W. Lin, T. S. Pan, M. C. Chen, Y. J. Yang, Y. Tai, F. F. Chen, *Appl. Phys. Lett.* 2011, 99, 023303.
[144] M. M. Rehman, G. U. Siddiqui, J. Z. Gul, S.-W. Kim, J. H. Lim, K. H. Choi, *Sci. Rep.* 2016, 6, 36195.
[145] W. T. Kim, J. H. Jung, T. W. Kim, *Appl. Phys. Lett.* 2009, 95, 222104.
[146] T. Carey, S. Cacovich, G. Divitini, J. Ren, A. Mansouri, J. M. Kim, C. Wang, C. Ducati, R. Sordan, F. Torrisi, *Nat. Commun.* 2017, 8, 1202.
[147] M. Yoshida, R. Suzuki, Y. Zhang, M. Nakano, Y. Iwasa, *Sci. Adv.* 2015, 1, 1500606.
[148] J. Li, Y. Zhao, H. S. Tan, Y. Guo, C. A. Di, G. Yu, Y. Liu, M. Lin, S. H. Lim, Y. Zhou, H. Su, B. S. Ong, *Sci. Rep.* 2012, 2, 754.
[149] Y. Qi, N. T. Jaffers, K. Lyons, C. M. Lee, H. Ahmad, M. C. McAlpine, *Nano Lett.* 2010, 10, 524.
[150] H. Tian, W. Mi, X.-F. Wang, H. Zhao, Q.-Y. Xie, C. Li, Y.-X. Li, Y. Yang, T.-L. Ren, *Nano Lett.* 2015, 15, 8013.
[151] H. B. Heersche, P. Jarillo-Herrero, B. Oostinga, L. M. K. Vandersypen, A. F. Morpurgo, *Nature* 2007, 446, 56.
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