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Solution-Processed Resistive Switching Memories based on Hybrid Organic-Inorganic Materials and Composites

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Resistive random-access memory (ReRAM) is expected to be the next-generation non-volatile memory device because of fast operation speed and low power consumption. Switching media in most ReRAM are oxides which are rigid and require high-temperature processing. Here, we review two emerging types of low-cost solution-processed ReRAMs with sandwich structure: one is hybrid nanocomposites with charge-trapping nanoparticles (NPs) embedded in polymer matrix, and the other is hybrid halide perovskite which have been intensively investigated recently for optoelectronic applications. We will review the recent developments on materials selection, device performance and operation mechanisms. Resistive switching in hybrid materials and composites is ubiquitous because of the abundant existence of charge-trapping defects and interfaces. The future challenges and potential breakthroughs will also be outlined.

Keywords: halide perovskite, resistive switching memory, filament, defects trapping

1. Introduction

Memories refer to systems in nature where their chemical and physical properties depend on the history of the systems. The operation of memory devices may involve different types of elementary particles like electrons, ions, photons and so on. Modern memory technologies have attracted lots of attentions because of wide-spread applications in digital and analog electronics, neutron network, data storage and artificial intelligence.¹ Among various types of memories, resistive switching (RS) devices are very promising, and ReRAM is considered as one of the most competitive next-generation non-volatile data storage devices.² Such memory devices possess advantages such as simple architecture, fast switching speed, good endurance and retention. Furthermore, the advancements in healthcare technology and the Internet of Things (IoT) demand flexible memories with high density and ultra-low power consumption.³

In the past decade, ReRAM research has been focused on inorganic materials such as SiO₂, TiO₂, Ta₂O₅, and so on.⁴ Such inorganic devices possess excellent memory performance and

can be integrated with high density. For example, in the work by Jo et al.,⁵ the amorphous-Si based device arrays (Figure 1a) are CMOS-compatible and offer promising characteristics such as fast writing (<10 ns), reasonable endurance (>10⁵ cycles) and

Figure 1 (a) SEM image of Si-based memristive nano-crosspoint devices with 50 nm half-pitch. Pt nanowires fabricated by nanoimprint lithography sandwich a 50-nm-thick TiO₂ insulating thin film. Reproduced with permission.⁵ (b) Schematic illustration of the concept of using memristors as synapses between neurons. Insets: schematics of the two-terminal device geometry and the layered structure of the memristor. Reproduced with permission.⁷

good retention time (~7 years).

Inorganic ReRAM cells can imitate synapses and exhibit analog switching behaviour.⁶ In one representative report, Jo et al. designed ReRAM cells made of co-sputtered Ag and Si active layers (Figure 1b),⁷ and the movement of interface between Ag-rich (high conductivity) and Ag-poor (low conductivity) regions gives rise to resistive switching. Authors demonstrated that the behaviour of hybrid CMOS-neuron/memristor-synapse circuit is similar to that of rat hippocampal neurons under electrical stimulations. But inorganic ReRAM devices are often rigid, which poses as a challenge when integrating with bio-systems

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like neurons and soft tissues in wearable devices. Furthermore, the processing of inorganic ReRAM is relatively expensive and requires high temperature.

Organic semiconductors are flexible and have been explored for electronic memories as early as 1970.⁸ In the last decade, organic resistive memory devices attracted a wide range of attention from scientists and engineers due to their excellent memory performance and low production cost.⁹ Besides organic and inorganic materials, hybrid organic-inorganic nanocomposites offer excellent device performance with high-mechanical flexibility, simple fabrication and low cost.¹⁰ Hybrid organic-inorganic halide perovskites have also attracted lots of attentions for photovoltaic and optoelectronic applications. These hybrid materials combine the superior properties of organic materials and inorganic materials. In the recent five years, the organic-inorganic halide perovskites have been explored for ReRAM applications. The remarkable electrical performances of such emerging materials such as non-destructive reading process, nonvolatility, high ON/OFF ratio, and fast switching speed meet the requirements for viable memory technologies.

Compared to inorganic memories, organic and hybrid materials have several key advantages. First, in terms of industry-scale manufacture, organic and hybrid memories have the huge advantage of low cost, ease of processing and simple device structures. As an attractive feature for industry-scale processing, hybrid materials and composites can be prepared at low temperatures using solution processing techniques such as spin coating, spray coating, ink-jet printing, and even blade coating. Second, the excellent flexibility of organic and hybrid materials allows the realization of emerging flexible devices, allowing foldable and wearable applications.¹¹ Finally, adding inorganic (either metal or oxides) NPs to form hybrid composites is promising to enhance the memory performance without compromising the physical properties.

2. General mechanisms of resistive switching

2.1 Nonlinear IV curves and the origins

Charge transport in semiconductor-metal heterostructures can be quite complex, involving Ohmic, Poole-Frenkel (PF), space charge-limited current (SCLC) and other mechanisms.¹² Several different mechanisms may exist in one device, and different mechanisms may dominate in different material systems. Particularly, when the electrode-semiconductor contact is ohmic, the accumulation of carriers near the electrode builds up a space charge, which limits the current injection.¹³ The resulting current is defined as SCLC, which gives important information regarding the carrier mobility and trap characteristics.

The I-V curves plotted in a log-log scale can provide important information about the conduction mechanism. When the voltage bias is low, the relationship between current and voltage follows the Ohm's law:¹⁴

$$J_{\text{ohm}} = qn\epsilon\mu \frac{V}{d}$$

where q is electron charge, n is the concentration of the free carriers in thermal equilibrium, ϵ is the dielectric constant, μ is the electronic mobility, and d is the thickness of the film. In this region, the density of injected carriers from the external circuit is smaller than the density of thermally generated free carriers inside the semiconductor, and the thermal generated free carriers act as the main conduction medium.

When the bias increases, the current could be dominated by the PF conduction, which is induced by the trapped carriers inside the film. The PF conduction follows the equation below:¹⁵

$$J_{\text{PF}} = qn\epsilon\mu \exp\left(\frac{-q(\Phi_B - \sqrt{qE/\pi\epsilon\epsilon_0})}{k_B T}\right)$$

where Φ_B is the effective barrier height, k_B is the Boltzmann constant, T is the absolute temperature and ϵ_0 is the permittivity of free space. In this region, the thermal excitation of electrons may emit from traps into the conduction band of the film.¹⁶ In some cases, this PF conduction region may not be observed.

In the high bias region, traps are filled and injected carriers are more dominant than thermally generated ones. The J-V curve of the trap-filled SCLC can be described as below:¹⁷

$$J_{\text{trap-filled}} = \frac{9}{8} n\epsilon\mu \left[\frac{V^2}{d^3}\right]$$

After all the traps are filled, the injected carriers can move freely inside the film, and the current therefore quickly jumps to high-current state, giving rise to current hysteresis.

Besides PF conduction and SCLC, other mechanisms like Schottky emission and ion conduction can also give rise to nonlinear IV curves. In the Schottky case, semiconductor and electrode do not form Ohmic contact, and the difference between the work function of metal electrode and the electron affinity of semiconductor leads to the formation of Schottky barriers.¹⁸ If there are lots of mobile ions, the ion current will interfere with the electronic current, and the ion trapping and carrier-carrier interaction can also result in nonlinear IV curve and current hysteresis.

2.2 Interface-type switching vs. filamentary-type switching

In the common RS memory structures, there are two back-to-back Schottky diodes. Figure 2a shows a typical RS device with Pt/TiO₂/Pt structure, and the active TiO₂ layer forms two diodes with the Pt electrodes.¹⁹ In a rectifying Schottky diode, there is a depletion region in the semiconductor near the interface, which gives the barrier a high resistance when small voltage biases are applied.¹⁸ Under a forward voltage bias, the electric current flowing through the barrier is essentially governed by the laws of thermionic emission. Under reverse bias, there is a small leakage current as some thermally excited electrons in the metal have enough energy to surmount the barrier. To first approximation this reverse current should be constant, but at very high biases, the Schottky diode breaks down.

In general, the Schottky barrier at the semiconductor/metal interface sensitively depends on multiple factors besides the difference of the work function of metal electrode and the electron affinity of semiconductor leads to the formation of Schottky barriers. Chemical termination of the semiconductor in the depletion region and the metal-induced gap states can

cause Fermi-level pinning and modify the Schottky barrier. In the interface-type RS, the resistance change is caused by field-induced modification of Schottky barrier homogeneously over the entire electrode area.² As shown in Figure 2b, in a typical RS operation, the device was switched ON by applying negative bias and OFF only by applying the opposite (positive) bias (this is the definition of a bipolar switch).¹⁹

In contrast, filament-type RS is inhomogeneous in nature, and the current conduction is highly confined to a small part of the device area.⁴ There could be many different types of metallic filaments whose formation and rupture can give rise to abrupt RS operation. The most common one is metallic bridges that result from the migration of metal atoms from electrodes (e.g., Ag and Cu) through the semiconductor films. This mechanism is general for organic, inorganic as well as hybrid materials. Figure 2c shows a typical current-voltage measurement and illustrates the switching processes occurring in an Ag/Ag-Ge-Se/Pt cell.²⁰ Actually, such metal dendrites were already reported in 1976 in a lateral Ag/Ag-As₂S₃/Ag structure,²¹ and the optical micrograph is shown in Figure 2d. The formation of conductive filaments (CFs) may involve redox reactions and electrochemical metallization. For organic semiconductors, carbon-rich filaments can be formed by the local heating and degradation. We should note that most defects in semiconductors are charged, and their electro-migration often can lead to the formation of conductive filaments. Although filament-type RS is quite common, the microscopic picture is often unclear. It is very hard to experimentally observe the binding of semiconductor atoms to metal ions and the position of binding sites, which are essential for the production and characteristics of metal filaments.

Figure 2 (a) An AFM image of nano-crosspoint devices with 50 nm half-pitch. Pt nanowires fabricated by nanoimprint lithography sandwich a 50-nm-thick TiO₂ insulating thin film. Reproduced with permission.¹⁹ (b) Experimental (solid) and modelled (dotted) switching I-V curves. Reproduced with permission.¹⁹ (c) I-V curve of a Cu/SiO₂/Pt electrochemical metallization cell. The insets show dynamics of metallic filament formation. Reproduced with permission.²⁰ (d) Optical microscopy image of an Ag dendrite grown from the (-) Au electrode towards to (+) Ag electrode within an As₂S₃ thin film on a glass substrate. Reproduced with permission.²¹

3. Hybrid composite memories based on organic polymers and inorganic NPs

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3.1 Overview of organic electronic memories

In the recent decades, organic electronic memories have attracted much attention due to their unique advantages such as low cost, easy processing and flexible compatibility.²² Organic memories include small molecules, polymers and composites.⁹ Small organic molecules have low molecular weight and can be deposited under high vacuum without decomposition by using thermal evaporation. Polymer molecules, on the other hand, consist of much larger molecules with long chains of repeating monomer units and will decompose before evaporation begins. Compared to molecules, polymers are more robust, and their uniform films are more suitable for device applications.²³

As an attractive feature for industry-scale processing, polymer materials can be prepared at low temperature using solution processing, such as spin coating, spray coating, ink-jet printing, and even blade coating. A typical structure for a hybrid organic/inorganic non-volatile memory device consists of composite organic molecules: metal/semiconductor NPs layer sandwiched between two metal electrodes. The device area is defined by the overlap between the top and the bottom electrodes; therefore, a very high memory density can be easily achieved by using cross-bar arrays. In the fabrication of such devices, care should be taken to avoid short circuit between the top and the bottom electrodes.

Furthermore, embedding polymers with functional NPs offers a new direction and more property tunability in non-volatile organic polymer memory. This method not only provides rich trap centers for charge trapping,²⁴ but also somehow produces a strong electric field to enhance the filament formation with better stability.^{25, 26} Such hybrid polymer/particle nanocomposite can combine the advantages of both inorganic materials and organic polymers.²⁷ Generally, hybrid inorganic/organic nanocomposites are composed of organic layers containing metal NPs, semiconductor quantum dots (QDs), core-shell semiconductor QDs, fullerenes, carbon nanotubes, graphene molecules or graphene oxides (GOs).¹⁰ Some representative examples on hybrid composite memories are given in Table 1. In fact, protein can be considered as a hybrid composite material because it often contains metal ions, and ferritin, a primary intracellular iron-storage protein, was used in RS memories.^{28, 29}

In terms of mechanism, charge transfer between the polymer matrix and nanoparticles apparently plays an important role. In general, Schottky emission is not the dominant one because there are more than one semiconductor/metal interface in such hybrid composites.

As a result of the organic matrix, such hybrid composite memories are highly flexible. Substrates such as poly-vinylidene difluoride (PVDF), polyethylene terephthalate (PET) and polyether sulfone (PES) can be used in flexible memory devices. In fact, there have been intensive research on flexible memory devices in recent years.³⁰⁻³⁵ Beside common polymer substrates, stainless steel could also be used as an alternative flexible

substrate because it has high corrosion resistance, high conductivity and thermal stability.³⁶

3.2 Polymer memories with metal NPs

The design principle of polymer nanocomposite memories is to use NPs to modulate the charge transport across the polymer matrix and to achieve optimal device performance. In terms of device fabrication, both polymer and NPs can be solution processed. To achieve desired performance, proper polymer and NP types should be selected. Metal particles are frequently used because they are excellent traps for carriers.

In 2004, Yang's group in UCLA demonstrated a high-performance memory made from a polystyrene (PS) film containing Au NPs and 8-hydroxyquinoline sandwiched between two metal electrodes.³⁷ This hybrid composite devices were fabricated via solution processing. As shown in Figure 3a, the Au NPs have a narrow size distribution (1.6–4.4 nm in diameter). Such device can be repeatedly written, read, and erased in air (Figure 3b), and the transition takes place in nanoseconds.³⁷ Authors attributed the electronic switching operation to the electric-field-induced charge transfer between the Au NPs and 8-hydroxyquinoline. Two years later, this group also reported a memory device composed of conjugated poly(3-hexylthiophene) (P3HT) and Au NPs capped with 1-dodecanethiol sandwiched between two metal electrodes.³⁸ In this work, authors attributed the electronic transition to an electric-field-induced charge transfer between Au NPs and P3HT.

In 2011, Choi's group reported a bistable organic memory device with Au NPs absorbed on a conducting poly-(N-vinylcarbazole) (PVK) colloids hybrid layer deposited on flexible poly(ethyleneterephthalate) (PET) substrates.³³ It showed the maximum on/off ratio of 10^5 due to large induced hole charges (5 holes/NP), a long retention stability of 10^6 s, and endurance to electrical stress above 1.5×10^5 cycles.

Besides homogeneous polymer films, polymer fibres were explored for memory applications. Tseng et al. reported a non-volatile memory based on nanofibers of conjugated polymer polyaniline decorated with Au NPs.³⁹ As a unique feature, a very short switching time of less than 25 ns was observed. Such fast operation has been rarely reported for hybrid memories. Like other reports, authors believe that the mechanism involves electric-field-induced charge transfer between polyaniline and Au NPs.

Besides devices involving Au NPs, Kim et al. demonstrated in 2010 a bistable device with hybrid composites of polymethyl methacrylate (PMMA) and Ag NPs.³² The device showed a maximum ON/OFF ratio of 4×10^3 and a large endurance above 7×10^4 cycles. There are very few reports on using NPs of metals other than Au and Ag in hybrid nanocomposite memories. In 2009, Park et al. reported a four-level non-volatile memory cells consisting of aluminium tris (8-hydroxyquinoline) (Alq_3) layer embedded with Ni NPs surrounded by NiO tunnelling barrier.⁴⁰ They presented an on/off ratio of 1×10^3 , a retention time of more than 10^5 s, an endurance of more than 5×10^2 cycles, and multilevel cell (MLC) operation.

3.3 Organic memories with oxide and chalcogenide NPs

Figure 3 (a) TEM image of Au NPs. (b) Write-read-erase cycles of the Al/Au-DT+8HQ+PS/Al device. W, R and E in the top figure mean write, read and erase, respectively. The labels '1' and '0' in the bottom figure indicate the device in the high and low conductivity states, respectively. Reproduced with permission.³⁷ (c) I-V curves of ITO/PVK: TiO_2 /Al and ITO/PVK/Al devices. The inset shows ON and OFF currents and ON/OFF ratio measured as a function of TiO_2 NP volume ratio. Reproduced with permission.⁴³ (d) I-V curve of the rGO/ MoS_2 -PVP/Al flexible memory device. The inset is the memory device structure. Reproduced with permission.³⁴

Similar to metal NPs, oxide and chalcogenide NPs were also used in polymer memories. In spite of weaker charge trapping capability, these non-metals offer many more choices than the metals in nanoparticle fabrication. In 2006, Kim et al. reported non-volatile organic bistable devices fabricated from Cu_2O nanocrystal embedded in a polyimide layer.⁴¹ Authors ascribe the electronic switching to the charge transfer from the polymer layer and the charge trapping in the Cu_2O NPs.

ZnO and TiO_2 NPs received lots of attentions in nanocomposite memory research. In 2009, Son et al. fabricated organic bistable devices by using ZnO NPs embedded in an insulating poly (methyl methacrylate) (PMMA) polymer layer on flexible polyethylene terephthalate (PET) substrates.³¹ The ON/OFF ratio is about 40. PMMA layers are good charge blocking material, and electrons are injected into the PMMA layer in the writing processes. At high bias, the SCLC process dominates and the injected electrons are captured in ZnO NPs, leading to large modulation of the junction resistance. In 2011, a mixture of ZnO NPs and PMMA was used as an active layer in a non-volatile resistive memory device.⁴² The device exhibited an ON/OFF ratio of 10^4 , retention time of $>10^5$ s, and number of readout of $>4 \times 10^4$ times under a read voltage of 0.5 V.

TiO_2 is an excellent electron acceptor in hybrid memory systems because of its low LUMO energy level (4.2 eV). In 2009, Cho et al. studied unipolar non-volatile memory devices based on composites of PVK and TiO_2 NPs.⁴³ Authors prepared two devices with ITO/PVK: TiO_2 NPs/Al and ITO/PVK/Al structure respectively. The devices with TiO_2 NPs showed a uniform cell-

to-cell switching, stable switching endurance, and a high retention time longer than 10^4 s, whereas structures without TiO_2 NPs did not show RS (Figure 3c). In the device, the OFF state was dominated by thermally activated behaviour, while the ON state followed tunnelling transport. Authors also claimed that the RS was closely associated with filamentary conduction. In 2014, Chen et al. reported that a novel sulphur-containing poly(o-hydroxy-imide) 3SOH-6FPI with pendant hydroxyl groups can be hybridized with TiO_2 and used for memory applications.⁴⁴ The resulting hybrid films having different TiO_2 concentrations from 0 wt.% to 50 wt.% exhibited electrically programmable digital memory properties from DRAM, SRAM, to WORM. Such devices have a very high ON/OFF current ratio (10^8), underscoring the excellent charge trapping ability of TiO_2 NPs. Besides oxides, researchers explored chalcogenide NPs as

charge traps in hybrid nanocomposite memory devices. In 2008, Son et al. fabricated a non-volatile hybrid nanocomposite memory by embedding inorganic CdSe/ZnS NPs into a conductive PVK polymer on a flexible substrate.³⁰ The ON/OFF ratio of such devices is quite low (<22) and no other performance parameters were given in this work. In 2012, Liu et al. reported a memory device made from MoS_2 - polyvinylpyrrolidone (PVP) nanocomposite with reduced graphene oxide (rGO) and Al electrodes (Figure 3d).³⁴ Amphiphilic PVP assists the exfoliation of MoS_2 and enables the dispersion in a wide range of solvents. The ON/OFF ratio of such devices is 10^2 . The study also claimed that the electrical transition mechanism is a result of charge trapping and detrapping of nanoscale MoS_2 on the PVP matrix.

Table 1. Summary of reported performance and the mechanism of hybrid composite memories based on organic polymers and inorganic NPs. Devices with oxide or chalcogenide are highlighted by grey shade.

Hybrid nanocomposite	Top-bottom electrodes	ON/OFF ratio	Endurance	Retention	Mechanism	Year	Ref.
PS + Au (w/ dodecanethiol)	Al-Al		Many times		Charge transfer	2004	37
xHTPA/Alq3/NPB/xBP9F + Mg/Ag/Al/Cr/Au	Al-Al/Cr/Cu/ITO /Au/Ni	20 - 10^6			Charge trapping and hopping	2005	45
polyaniline nanofibers + Au NPs	Al-Al	20		Several days	Charge transfer	2005	39
PI + Cu_2O	Al-Al				Charge trapping and hopping	2006	41
P3HT + Au NPs	Al-Al		1500	3 days	Poole-Frenkel emission	2006	38
PEDT/Au-PEDT/PEDT	Au-Au					2007	46
Pentacene + Au NPs + 3-aminopropyl-triethoxysilane	Au-Si				charge trapping/ detrapping	2007	47
PVK + CdSe/ZnS NPs	Al-ITO	3.7-22.5				2008	30
Alq3/ (Ni nanocrystals surrounded by NiO)/Alq3	Al-Al	10^3	5×10^2	10^5 s	SCLC F-N tunneling	2009	40
PVK + TiO_2	Al- ITO	10^5		10^4 s	filamentary conduction and tunneling transport	2009	43
PMMA + ZnO	Al/-ITO	10^4	4×10^4	10^5 s		2011	42
PVK + Au NPs	Al-ITO	10^5	1.5×10^5	10^6 s	SCLC	2011	33
PVP + MoS_2	rGO-Al	10^2				2012	34
3SOH-6FPI + TiO_2	Al-ITO	10^8				2014	44
Fibroin + Au	Ag-Au+Cr	10^7		4.5×10^3 s		2015	29

4. Hybrid perovskite memories

4.1 Overview of hybrid perovskites for memory applications

Hybrid perovskite materials have attracted lots of attentions due to its bandgap tunability, high light absorption, long charge diffusion length, and dielectric polarization properties.⁴⁸ In optoelectronic devices, it has been proposed that the reversible ion migration can modulate the photocurrent.⁴⁹ Furthermore, the organic cation of perovskite may rotate to show ferroelectric behaviour.⁵⁰ Under an applied electrical field, ion migration and cation rotation could enable the operation of perovskite-based ReRAM. Indeed, the first ReRAM based on hybrid perovskite was reported by Yoo et al. in 2015. These hybrid perovskite materials promise the excellent resistive switching behaviours in terms of endurance, high retention time and high ON/OFF ratio.⁵¹

Moreover, the structural flexibility and low-temperature processability of hybrid perovskites is promising for industrial manufacturing of wearable devices.⁵² For example, Gu et al. reported a flexible perovskite device on PET substrates. Authors demonstrated reliable electrical performances under a bending radius of 1.5 cm.⁵³ In the work by Choi et al., all-inorganic perovskite layers were prepared on a cyclo-olefin polymer substrates.⁵⁴ A high ON/OFF ratio around $10^6 \sim 10^7$ was observed under bending radii of a few mm.

The operation mechanisms in perovskite ReRAM sensitively depend on material selection and physical properties. In general, there are two main types of ReRAM. In the interface type, ion transfer near the interface of electrode and semiconductor modulate the Schottky barrier and the resistive states, while in the filamentary type, the formation and rupture of CFs give rise to the memory action. The Table 2 exhibits some representative research works in recent years. In the filamentary type, the ON state should exhibit the simple Ohmic transport behaviour, while the transport in the interface type is usually dominated by Schottky emission. In addition, mechanisms like phase transition were also mentioned in perovskite-based memories.⁵⁵

4.2 Interface-type perovskite memories

In 2015, Yoo et al. reported the first application of hybrid perovskites in memory devices.⁵¹ They designed a simple capacitor configuration (metal–dielectric–metal) consisting of Au/CH₃NH₃PbI_{3-x}Cl_x/fluorine-doped tin oxide (FTO) substrate (Figure 4a). As shown in Figure 4b, the device showed typical resistive switching behaviours with low operation voltage (set voltage around 0.8 V), stable endurance (>100 times), and long retention time (>10⁴ s). Authors suggested the mechanism of RS behaviours is related to trap-controlled SCLC. Because most traps may be located at the perovskite/electrode interface, this device is most likely interface type.

In another work, Lin et al. reported a memory with sandwiched indium-doped tin oxide (ITO)/PEDOT: PSS/CH₃NH₃PbI₃/Cu structure and used the device as a logic OR gate. This structure shows excellent electrically performances, such

as outstanding ON/OFF ratio (10^4), long retention time (10^4 s) and 3000 endurance cycles.⁵⁶ For the mechanism, authors claimed that charge trapping on the point defects changed the Schottky barriers at the perovskite/PEDOS: PSS interface. This work leveraged on the photo-responsive nature of perovskites to enable logic gates with light and voltage as inputs, which may help develop perovskite-based logic circuit and optical computation applications.

In 2017, our group reported a hybrid perovskite memory structure with an MAPbBr₃ (CH₃NH₃PbBr₃) layer sandwiched between Au and ITO electrodes.⁵⁷ Special cares were taken to make the active layer uniform and smooth in order to reduce the defects and to improve the reliability. High ON/OFF ratio, high electric endurance over 10^3 cycles, and a high retention time (10^4 s) were observed. We believe that the ion migration at the perovskite/ITO interface is the reason behind the good device performances. Using electron microscope, we also discovered the gradual distribution of MA vacancies in the perovskite layer, which should be taken into accounting to explain the RS behaviour in perovskite devices.

Figure 4 (a) Structure of Au/CH₃NH₃PbI_{3-x}Cl_x/FTO device. (b) I-V curves of the device at first measurement and after sweeping 100 times. Reproduced with permission.⁵¹ (c) I-V characterization of the flexible Au/CH₃NH₃PbI₃/ITO/PET device with different bending cycles. Reproduced with permission.⁵³ (d) I-V curves of Ag/MAPbI₃/FTO devices with different perovskite layer thicknesses. Reproduced with permission.⁷⁶

4.3 Filament-type perovskite memories

Most hybrid perovskite memories are regarded as filamentary type. Using electrochemical active metal like Ag, Al and Cu as electrodes, is a common approach to induce filament-type RS. In 2016, using a structure of FTO/TiO₂/CH₃NH₃PbCl_{3-x}I_{3-x}/Al, Yan et al. reported a memory device showing a very high ON/OFF ratio of 10^9 .⁵⁸ The authors attributed the memristive properties to the formation and rupture of metallic filament in the hybrid perovskite layer. In 2016, Yoo et al. demonstrated a memory device with CH₃NH₃PbCl_{3-x}I_{3-x} layer sandwiched between Ag and FTO electrodes.⁵⁹ The RS behaviours can be explained by formation and rupture of Ag CF. Such devices showed reliable endurance over 10^3 times and a retention time of 10^4 s, which revealed their potential for neuromorphic computing applications.

Table 1. Summary of reported performance and the mechanism of perovskite resistive switching devices. Devices with possible interface-type mechanism are highlighted by grey shade.

Perovskite	Top-bottom electrodes	Endurance (times)	Retention (s)	ON/OFF ratio	Mechanism	Year	Ref.
CH ₃ NH ₃ PbI _{3-x} Cl _x	Au-FTO	100	10 ⁴	≈ 3	Interface-type	2015	51
CH ₃ NH ₃ PbI ₃	Cu-ITO (PEDOT:PSS)	3000	3 × 10 ⁴	10 ⁴	Interface-type	2015	60
CH ₃ NH ₃ PbI _{3-x} Cl _x	Al-FTO	—	—	10 ⁹	CF (Al)	2016	58
CH ₃ NH ₃ PbI ₃	Ag/Ni-Pt	350	1.1 × 10 ³	10 ⁶	CF (I ⁺)	2016	61
CH ₃ NH ₃ PbI ₃	Au-ITO	400	10 ⁴	≈ 10	CF (V ⁺ _I)	2016	53
CH ₃ NH ₃ PbCl _{1-x} I _{3-x}	Au-Ti(TiO ₂)	—	2.5 × 10 ⁴	≈ 20	Interface-type	2016	62
CH ₃ NH ₃ PbBr _{3-x} Cl _x	Ag-FTO	250	10 ³	10 ³	Interface-type	2016	63
CH ₃ NH ₃ PbI _{3-x} Cl _x	Ag-FTO	10 ³	4 × 10 ⁴	≈ 10 ²	CF (Ag)	2016	59
CsPbBr ₃	Ni(ZnO)-FTO	100	10 ⁴	10 ⁵	Interface-type	2016	64
CsPbBr ₃	Al-ITO(PEDOT:PSS+PET)	50	—	10 ²	CF (Al or Brion)	2017	65
CH ₃ NH ₃ PbI _{3-x} Br _x (x = 0,1,2,3)	Au-ITO	30	10 ⁴	10 ²	CF (V ⁺ _I and V ⁺ _{Br})	2017	66
CH ₃ NH ₃ PbI _x	Au-Pt	500	>10 ⁵	>10 ³	—	2017	67
CH ₃ NH ₃ PbI ₃	Ag/Au-Au	10 ³	706 (38)	≈ 10 ⁷	CF (V ⁺ _I)	2017	68
CH ₃ NH ₃ PbI ₃	Au (ZnO)-ITO	100	10 ⁴	≈ 10 ²	CF (V ⁺ _I)	2017	69
CH ₃ NH ₃ PbI ₃	Ag-Pt	1338	29 800	10 ⁶	CF (Ag)	2017	54
BA ₂ MA _{n-1} PbI _{3n+1} (n = 1, 2, 3 and ∞)	Ag-Pt	250	10 ³	≈ 10 ⁷	CF (Ag)	2017	70
CH ₃ NH ₃ PbI ₃	Au-ITO	> 600	>10 ⁴	>10	—	2017	71
CH ₃ NH ₃ PbBr ₃	Au-ITO	10 ³	10 ⁴	10 ³	Interface-type	2017	72
CsPbI ₃	Ag- Pt	> 300	10 ³	>10 ⁶	CF (Ag)	2017	73
(PEA) ₂ PbBr ₄	Au-graphene	—	—	10	CF(Br)	2017	74
CsPbBr ₃	Ag-ITO(PEDOT: PSS)	300	—	< 10	CF (Ag)	2018	75
CH ₃ NH ₃ PbI ₃	Ag-FTO	10 ³	10 ⁵	10 ⁶	CF (Ag & V ⁺ _I)	2018	76

In addition to metallic filaments, vacancy defects (V_{Pb}, V_{MA}, and V_I) are also able to form CFs. In 2016, Choi et al. reported a memory structure with a CH₃NH₃PbI₃ layer sandwiched between Ag and Pt electrodes.⁶¹ Authors demonstrated that such device showed excellent properties such as low SET voltages below 0.15 V, and high ON/OFF ratio (10⁶). The mechanism of such filament type device was proposed to be related to the migration of anion defects (iodine interstitials and vacancies) with low activation energy. But the possibility of forming Ag filaments was not excluded. In the same year, Gu et al. reported a highly flexible Au/CH₃NH₃PbI₃/ITO/PET memory device structure.⁵³ Authors claimed that the mechanism of RS behaviour is the migration of iodide (I) vacancies and subsequent formation of vacancy CF. As shown in Figure 4c,

such devices maintained reliable and uniform memory operations either in tensile bending state or in compressive bending state. In 2017, Hwang et al. demonstrated Au/ZnO/CH₃NH₃PbI₃/ITO and Al/AlO_x/CH₃NH₃PbI₃/ITO memory device structures, and the authors attributed RS behaviours to the migration of I vacancy defects.⁶⁹ Furthermore, such devices showed reliable electrical properties for 30 days in ambient air. Authors pointed out that the ZnO and AlO_x layers help protect the perovskite layer from moisture and improve the device stability.

In some reports, more than one type of CFs were invoked to explain the RS. In 2017, Liu et al. reported an all-inorganic based flexible memory with an Al/CsPbBr₃/PEDOT: PSS/ITO/PET structure.⁶⁵ Such structure maintained stable ON/OFF ratio of

10^2 under bending. Authors claimed that either Al CF or Br ion CF may be responsible for the RS behaviours, but it is not clear if nanostructures of Br ions can effectively transport current. In some works, other types of metallic filaments based on defects like vacancies were also reported. In 2018, Sun et al. reported a memory with the structure of Ag/MAPbI₃/FTO (inset in Figure 4d) and claimed the coexistence of two types of CFs.⁷⁶ From I–V curves of Ag/MAPbI₃/FTO memory cells with different thicknesses of MAPbI₃ (Figure 4d), authors pointed out that the RS performance is decided by the thickness-dependent competition of metallic (Ag) and vacancy defect (I) filaments. Such structure showed different ON/OFF ratio from 10^4 to 10^6 . But, in general, it remains challenging to experimentally observe such nanoscale CFs, and as a result care must be taken to ensure device reliability.

Artificial synapses based on RS devices are expected to exhibit short-term behavior for computations and long-term behavior for learning and memory.⁷⁷ In a very recent work, Tian et al. reported that 2D Ruddlesden–Popper phase hybrid lead bromide perovskite single crystals are promising for memory applications.⁷⁴ The vertical graphene/(PEA)₂PbBr₄/Au structure showed extremely low operation current (10 pA) and 400 fJ/spike synaptic operation, which is very close to the energy consumption of biological synapses. Authors believed that the mechanism behind the RS is the Br[−] ion migration which leads to formation and rupture of CFs.

5. Conclusion and outlook

We reviewed two classes of hybrid systems for non-volatile memory applications: one is hybrid composites of polymers imbedded with nanoparticles and the other is hybrid perovskites. RS appears to be ubiquitous in such hybrid composites and materials. This is because charge-trapping defects are ubiquitous in such materials with high complexity. Both material systems are amicable to solution processing and promising for low-cost industrial manufacture. Furthermore, their compositions are much tunable than conventional materials, which offers new opportunities in material design.

In the polymer/nanoparticle composites, besides the materials mentioned in the review, there are other materials that can be explored. For example, many oxides with rich structures and physical properties exhibit resistive switching by themselves,^{78–81} which is an advantage for fabricating composite memories. Furthermore, the imbedded nanoparticles can be ferroelectric and even multiferroic.^{82, 83} In fact, the polymer matrix can also be ferroelectric.^{84–86} It is likely that the non-volatile character of hybrid RS memories can be enhanced using ferroelectric materials. In the field of memory research, the potential of such polymer/nanoparticle composites has not been sufficiently realized. Particularly, the dependence of RS performance on the density/size/shape/material of NPs is expected to be investigated in future studies.

In terms of preparation methods, almost all the works on hybrid memories so far have used spin coating to prepare the switching layers. However, more solution-processing methods

such as spray coating, ink-jet printing, and even blade coating can be explored. These preparation methods have been successful in fabricating optoelectronic devices and they have potential to be applied in memory fabrication. For example, the slot-die coating method can minimize material loss and reduce cost in industrial roll-to-roll manufacture.⁸⁷ Methods like doctor-blade coating are also promising for large-area production of uniform hybrid perovskite films.⁸⁸

Besides the active hybrid materials, device configuration and electrode characters can be explored to optimize the performance of hybrid RS devices. One promising direction is to explore new device configurations, particularly the lateral one with switching media being exposed.⁸⁹ On the one hand, the lateral structure makes it easier to modulate the device parameters and then change the switching properties; On the other hand, the special lateral structure has better sensitivity to environment conditions, like light and moisture. Furthermore, different electrode materials and morphologies can be tested to investigate the effects on charge injection and modulate the interface barrier.⁹⁰

Although RS appears to be ubiquitous in hybrid materials, the criteria for constructing hybrid RS memories with the optimal performance remain unclear. For inorganic oxides, the drift of oxygen vacancies under electric field often plays an important role in RS mechanism,⁹¹ but for hybrid memories energy band alignment and charge transport across organic/inorganic interfaces must be considered. In organic/nanoparticle composites, charge transport in organic matrix occurs simultaneously with charge trapping and detrapping in the nanoparticles, while in hybrid perovskite the charge transport along the Pb–I networks is modulated by the organic components. In order to advance such hybrid memories, future research is required to elucidate the fundamental transport properties in hybrid materials and composites.

Finally, we should note that although hybrid memory devices have lots of potentials for development, the biggest concern is their stability in ambient conditions. Hybrid perovskites break down quickly with exposure to ambient factors like humidity and light, and chemical decomposition and phase separation can cause the failure of devices.^{92, 93} Developing strategies to improve the ambient stability of hybrid perovskites is an active area of ongoing research. In fact, interfacing metallic oxide or carbon materials were reported to make hybrid perovskites more robust,^{94, 95} which will likely be explored in the context of hybrid memory devices. Insights from previous research works on the interaction of oxides such as SrTiO₃ and SiO_x with water and oxygen molecules may benefit the investigation of hybrid perovskites.^{96–98} Techniques like isotope labelling in a N₂/H₂ ¹⁸O tracer gas atmosphere combined with time-of-flight secondary-ion mass spectrometry could be explored to elucidate the underlying mechanism.⁹⁸ Hybrid nanocomposites with polymers and particles are more stable than hybrid perovskites, but their device stability has not been reported. Most polymers can survive temperatures up to 200–300 °C, and it will be interesting to investigate if their nanocomposites with nanoparticles become more stable. In addition, engineering the device structure and applying encapsulation are expected to

improve the device stability in air.⁹⁷ After stability and reliability issues are resolved, such solution-processed hybrid composites and materials are promising to find wide-spread applications in low-cost flexible non-volatile RS memories.

Conflicts of interest

There are no conflicts to declare.

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The acknowledgements come at the end of an article after the conclusions and before the notes and references.

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