Electrode Engineering in Halide Perovskite Electronics: Plenty of Room at the Interfaces

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Contact engineering is a prerequisite for achieving desirable functionality and performance of semiconductor electronics, which is particularly critical for organic–inorganic hybrid halide perovskites due to their ionic nature and highly reactive interfaces. Although the interfaces between perovskites and charge-transporting layers have attracted lots of attention due to the photovoltaic and light-emitting diode applications, achieving reliable perovskite/electrode contacts for electronic devices, such as transistors and memories, remains as a bottleneck. Herein, a critical review on the elusive nature of perovskite/electrode interfaces with a focus on the interfacial electrochemistry effects is presented. The basic guidelines of electrode selection are given for establishing non-polarized interfaces and optimal energy level alignment for perovskite materials. Furthermore, state-of-the-art strategies on interface-related electrode engineering are reviewed and discussed, which aim at achieving ohmic transport and eliminating hysteresis in perovskite devices. The role and multiple functionalities of self-assembled monolayers that offer achieving ohmic transport and eliminating hysteresis in perovskite devices.

1. Introduction

Organic–inorganic hybrid halide perovskites with general formula of APbX3 (A = MA, FA, and Cs; X = Cl, Br, and I) have become the fastest-advanced solar photovoltaic in recent years.[1–9] Owing to their extraordinary optical and electronic properties, such as high optical absorption, intense luminescence, ambipolar mobility, and long carrier lifetime, perovskites are able to realize mutual transformation between photons and carriers with high efficiency, thereby exhibiting munificent potential in diverse applications besides photovoltaic, including light-emitting diodes (LEDs),[10–13] lasers,[14–17] transistors,[18–21] detectors,[22–25] and photoelectrochemical catalysis.[26–29] However, the Achilles' heel of perovskite electronics is unreliable contacts due to intricate interfacial effects between perovskite and contact electrodes. Unlike most inorganic semiconductors (ISC) and organic semiconductors (OSC) that create solid via covalent bonds or van der Waals force, hybrid perovskites are featured with ionic bonds between A+ and PbX− framework, thus featuring high polarity and chemical reactivity.[30,31] Consequently, perovskites are unstable when they are exposed to moisture and oxygen in the atmosphere and can even be degraded by materials with moderate polarity.[32,33] The ionic nature of hybrid perovskites and the associated high reactivity tremendously hinder the development of reliable perovskite contacts, and intensive efforts have been undertaken to investigate the perovskite interfaces aiming to ultimately accomplish desirable contacts with suppressed chemical reaction and interfacial defect states.[34]

From the electronic engineering perspective, the success of new materials highly depends on the capability to design and fabricate desirable contact for the devices enabled by these materials. Since organic–inorganic perovskites possess hybrid characteristics, the state-of-the-art knowledge on the contact engineering of ISCs and OSCs can be consulted to advance the perovskite interfaces. For conventional ISCs, the energy band alignment at the semiconductor/metal interface is the most crucial factor affecting the junction barrier. Ohmic contact allows charge carriers to pass through the junction interface without scattering loss, thus improving the charge extraction as well as the device efficiency.[35] For electronic applications relying on the existence of internal electric field such as, solar cell, transistor, diode, etc., it is crucial to obtain non-ohmic contacts, including p–n junction, Schottky and other types of rectifying heterojunction.[36] In some cases, the image force and surface-states induced Fermi level pinning lead to charge rearrangement at the ISC contact interface.[37–39] Generally speaking, for both ohmic and Schottky devices, fabrication of a clean defect-free interface is the prerequisite to
realizing efficient contact for charge extraction with low contact resistance.\textsuperscript{[40]}

The junction interface between OSCs and electrode materials is more complicated than the ISC counterpart. Because solid-phase OSCs are formed via van der Waals force, the molecular interactions are weak with large inter-molecule distance.\textsuperscript{[42]} This character makes OSCs, especially their surfaces, unstable since electrons that could be photo-excited are easily captured by moisture or oxygen when they hop between adjacent molecules.\textsuperscript{[42]} Additionally, when OSCs are contacted with electronegative materials, undesired interfacial reactions may occur, including redox reaction, interface dipole formation, and orientation change of polar molecules, which drastically hampers the carrier transport.\textsuperscript{[43]} For metal contact, it has been reported that metal atoms are able to diffuse into OSC through the intermolecular pathways.\textsuperscript{[44]} To avoid the metal diffusion and direct damage of the organic layer, slow evaporation and “soft landing” approaches such as transfer printing were exploited for the fabrication of OSC contact.\textsuperscript{[45,46]} However, these methods cannot prevent the interface reaction or ion exchange for highly reactive contacts. As a result, self-assembled monolayer (SAM) was proposed and became a versatile and effective strategy for preparing the carrier injection contact to OSC. SAM inserted between metal electrode and OSC can effectively prevent interfacial chemical reaction and promote carrier transmission across the junction interface, thereby improving the performance of functional OSC devices.\textsuperscript{[47,48]}

The combination of hybrid character and unique ionic lattice puts perovskites in a new category of semiconductors different from ISC and OSCs. Similar to conventional semiconductors, the energy level alignment between perovskites and electrode materials plays a vital role in determining the contact property. The energy levels of commonly studied perovskites, metals, and conductive metal oxide electrodes are depicted in Figure 1. Understanding the energy alignment helps to choose suitable electrodes for perovskite contact, but, unfortunately, it only provides a blurry picture of the complex interfaces since other interfacial effects, such as electrochemical reaction, Fermi level pinning, and ion accumulation, may arise as a result of the ionic nature of perovskites.\textsuperscript{[49,50]} Unlike OSCs, which are usually passively degraded by electronegative contact materials, the halide ions at perovskite surface play a more active role in redox reactions and can even etch the contact electrodes.\textsuperscript{[51,52]}

The derived interfacial effects and electrochemical reactions make perovskite interface perplexed and engenders substantial impacts on device functionality, performance, and stability.\textsuperscript{[53]} Therefore, the implementation of contact engineering is especially important for perovskite materials to minimize undesired interfacial reactions and to pursue reliable contact properties.\textsuperscript{[54]}

In this focused review, we aim to present a comprehensive view of the interfacial electrochemistry and state-of-the-art strategies of contact engineering between perovskite and electrode materials. Due to the rapid development of perovskite solar cells (PSCs),\textsuperscript{[55–60]} the existing reviews in literature mostly focus on contact interfaces between perovskites and charge-transporting materials (i.e., the electron-transport layer (ETL) and the hole-transport layer (HTL)).\textsuperscript{[61–64]} While this review will discuss perovskite contacts in the context of electronic applications, which have received growing attention in recent years.

The design rules of perovskite contact for photovoltaic solar cells and typical electronics are fundamentally different. Solar cells require efficient electron and hole extraction with built-in potentials, which can be achieved by adopting ETL and HTL to construct n–i–p or p–i–n configurations. While for perovskite electronics, such as transistor, memory and detector, the built-in potential at the interfaces may not be preferred; instead, for most electronic applications, ohmic contact with bidirectional transport capability and low contact resistance is pursued to maximize the device performance without scattering loss. In perovskite electronics, ETL and HTL are usually not used, and the perovskite layer makes direct contact with the electrode, or an ultrathin layer is inserted at the interface to improve device performance. Besides typical perovskite electronics with metal–semiconductor–metal (MSM) structures (Figure 2a–c), HTL-free PSCs will be included in this review because the perovskite layers are directly contacted by electrodes (Figure 2d) and the related literature helps the understanding of perovskite/electrode interface. Besides the basic configurations, intricate designs of materials or heterostructures may be involved in specific devices such as ferroelectric transistors, charge-trapping...

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\caption{Energy levels of commonly studied halide perovskites, metals, and oxide electrodes. FAMAPb(I,Br) represents FA\textsubscript{0.85}MA\textsubscript{0.15}PbI\textsubscript{2.55}Br\textsubscript{0.45}. The energy levels of the perovskites are taken from refs. [49,50]. The green dashed lines indicate the prevalent trap levels in monohalide perovskites as reported in the literature.\textsuperscript{[55–60]}}
\end{figure}
transistors, synaptic transistors, photonic memories, visual memories, and light-emitting memories.\cite{65–70}

In the next section, we will first discuss the properties of perovskite/electrode interface and key factors in electrode engineering. Interfacial phenomena and adverse effects, including recombination reaction, ionic migration and diffusion, contact-related ionic migration, and ion accumulation, are reviewed to provide insights into the perovskite interfaces. Furthermore, we will discuss energy level alignment and possible effects upon perovskite surfaces, such as, surface band bending and contact-induced Fermi level offset. After reviewing the characteristics of perovskite interfaces, perspectives on potential contact-optimization strategies are given to address critical interfacial issues in perovskite electronics. In Sections 3 and 4, we will present the possible solutions for achieving ohmic contact and hysteresis-free interface, respectively. Electrode selection and contact engineering strategies are elaborated here for establishing non-reactive and reliable perovskite contact. In Section 5, we will introduce the role of SAMs and review their multiple functionalities in perovskite electronics. As a powerful interface engineering technique, the successful applications of SAMs in OSC devices and the lessons learned can be transferred to perovskite electronics, which provides promising configurations to pursue optimal perovskite/electrode contact. Finally, outlooks on electrode contact engineering toward high performance and stable perovskite optoelectronics are given.

2. Perovskite/Contact Interface and Key Factors in Electrode Engineering

Perovskite interface contains rich electrochemistry as a result of the ionic bonding in the cubic lattice, which features large electronegativity differences between atoms leading to a high tendency of Lewis acid–base reaction when contacting other materials.\cite{71} Unfortunately, the electrochemical reaction induced impurities can cause huge impacts on perovskite devices and even bury the intrinsic performance. In general, charge recombination and point defects at perovskite contact interfaces would significantly contribute to the degradation of device performance.\cite{73,74} As an example, Zarazua et al. employed impedance spectroscopy to investigate the interfacial nonradiative recombination and observed huge thermodynamical losses harming carrier collection in perovskite devices.\cite{75} The interfacial decomposition also arouses stability issues, hindering the industry-scale perovskite applications. In this section, we review the important interfacial effects and electrochemistry to build the foundation for perovskite contact engineering. Besides metal and oxide electrodes, this section will touch on other n- and p-type transporting materials, which can give us the full picture of perovskite interface characteristics.

2.1. Interfacial Chemical Reaction

The occurrence of interfacial chemical reaction at perovskite contacts has been considered as a bottleneck directly affecting the stability and long-term reliability of perovskite optoelectronics.\cite{76} Unlike PSCs using additional ETL and HTL to facilitate charge transport, perovskite electronics usually require direct contact between perovskite and electrodes, yielding complex chemistry and surface effects at the junction interface. Metals are the ubiquitous electrode materials for perovskite devices, but the presence of serious interfacial reactions has been reported to hamper electronic performance. Furthermore, the electrode reactions may degrade perovskite devices over time and even completely destroy them in a few hours under high humidity, thermal environment, or continuous operation.\cite{77–79} In principle, three kinds of adverse effects play significant roles in perovskite/metal interfaces: i) local interfacial redox reaction, ii) metal-ion migration into the perovskite,
As the prototypical noble metal, Au is the most widely used electrode material in perovskite research. However, detailed investigations disclosed severe electrochemical reactions between Au and perovskites although Au is often regarded for high resistance to corrosion and oxidation. As an example, Kerner et al. employed X-ray photoemission spectroscopy (XPS) to probe the MAPbI₃/Au interface. The variation of oxidation states and interface compositions confirm the volatilization of HI and catalyzed degradation of I₂, leading to the interfacial underpotential deposition of Pb⁰. The interfacial redox reaction can substantially deteriorate the device performance and sometimes even sabotage the intended application. In a photovoltaic experiment, underpotential deposition-induced Pb⁰ unexpectedly transforms the anodic Au to a cathode. Similar anode and cathode switching at perovskite/Au interfaces upon voltage bias were also observed by several groups as a result of strong interfacial electrochemical reactions.

It should be noted that the extent of electrochemical reaction at perovskite/Au interfaces depends on synthesis details. Liu et al. performed in situ observation of Au deposition on MAPbI₃ surface using a suite of spectroscopic techniques (i.e., ultraviolet photoelectron spectroscopy (UPS), inverse photoemission spectroscopy (IPES), and XPS). The XPS data are shown in Figure 3a. At the initial deposition stage with low Au coverage (<8 Å), the Au particles are slightly negatively charged. This charging effect is eliminated after the formation of an interconnection layer with more Au coverage. At an Au thickness of 64 Å, the hole accumulation with a built-in potential of 0.4 eV was found near the MAPbI₃ surface, indicating a p-doping effect generated by the Au electrode. In such a fresh MAPbI₃/Au interface measured in vacuum and dark, no strong redox chemical reaction was observed from the XPS measurement. Nevertheless, environmental factors, such as, light, heat, oxygen, moisture, and bias voltage, may trigger the interfacial reaction, leading to the degradation of device performance over time. Pospisil et al. reported the formation of gold halides under electrical biasing. When the Au electrode is positively polarized, the accumulated holes tend to oxidize the Au and produce gold halide species and halide vacancies VX⁺ in the vicinity of electrode (Figure 3b). Shlenskaya et al. also reported light-induced redox reactions at MAPbI₃/Au interface. Their X-ray diffraction (XRD) study revealed that the perovskite tends to release volatile I₂ and MAI upon light illumination and leads to the formation of reactive polyiodide melts. The reactive melts can further oxidize the Au electrode to produce gold halide compounds and alter the interface property. It should be noted that impurities and interface states as a result of the redox reactions are usually charged and can cause significantly interface...
scattering and nonradiative recombination, thus hindering the device performance and stability.

The migration of metal ions into the perovskite layer is also problematic. Halide perovskites are classified as semisoft materials as a result of their elastic property and soft Pb–X lattice. The soft nature of perovskites is a double-edged sword: it not only makes perovskites highly defect tolerant but also accelerates the diffusion of mobile ions and charged impurities in the perovskite lattice. The metal ions produced by interfacial redox reaction may diffuse into perovskite and degrade the device performance once the kinetic diffusion barrier is overcome. Ming et al. have estimated the diffusion barrier of different metal impurities in MAPbI₃ using first-principles computation (Figure 3c), leading to the conclusion that the metal ions with higher charge states generally possess higher kinetic barrier. This analysis is reasonable since higher charged metal cations tend to coordinate with more halide anions to generate complex compounds, and higher energy is needed to break the ionic bonds for the metal ion to migrate. According to the calculation result, commonly used metal electrodes, including Au, Ag, and Cu, are monovalent and can easily migrate in MAPbI₃, which is consistent with experimental reports. It is worth noting that the harms of metal ions on perovskite lattice depend on the characteristics of generated trapping defects. For example, the 3d energy level of Au can interact with Pb vacancies to form deep trap states that significantly damage perovskite performance, while Ag-3d and Cu-4d tend to form shallow impurity defects due to mild crystal field. This can also explain why the Cu contact does not cause considerable degradation in power conversion efficiency, as recognized by the PSC community. In a representative research reported by Zhao et al., even when Cu electrode directly contacted perovskite in the inverted PSC (indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)/MAPbI₃/Cu), the device still showed high efficiency of over 20%, indicating the benign nature of Cu complexes. Nevertheless, the diffusion of other metal ions, such as Au, may produce detrimental deep centers, which should be prevented to enable propitious charge transport in perovskites.

Another consequence of interfacial redox reaction is the corrosion of metal electrodes. In an XPS investigation, the iodine-containing species was found to react with Ag electrode to form AgI, leading to the corrosion of the metal electrode over time. In a more extensive electrode study, the corrosion of Ca, Al, Ag, and Au electrodes in perovskite devices as a result of halide ions redox reactions was recorded using scanning electron microscopy (SEM). As shown in Figure 3d, the corrosion process usually produces numerous voids and cracks within the metal layer, which allows further diffusion of halide species and causes severe destruction. To further understand this phenomenon, Zhao et al. immersed Al films into PbI₂ and MAI solutions. Intriguingly, the metal corrosion was observed in PbI₂ solution, while in MAI, no apparent change was observed, which leads to the conclusion that I⁻ and Pb²⁺ synergistically corrode the Al electrode. Moreover, it is found that the moistures play a role in facilitating ion diffusion, leading to an accelerated redox corrosion process. To eliminate the undesirable corrosion effects, interface engineering has been intensively pursued. It was shown that the use of chemically modified electrodes could effectively suppress the electrode corrosion. For example, Guerrero et al. introduced the use of Cr₂O₃/Cr electrode instead of pure metals, which exhibited strong resistance against oxidative corrosion. Another strategy is to adopt a contact interlayer to shield the electrode. Sanehira et al. reported that a MoO₃ interlayer could protect the underlying metal electrodes from halide corrosion. Generally speaking, with the proper control of contact resistance, the utilization of intermixed contact layer can offer numerous benefits, including reduction of interfacial recombination, efficient charge transport, and suppressed I–V hysteresis, which will comprehensively discuss in a later section of this review.

Besides metals, oxide electrodes and organic compounds can also react with halide perovskites to form complex bonding and derived adsorbates at the interface. In one representative work, Olthof et al. deposited 3 nm-thick CH₃NH₂₃PbI₃ films on MoO₃, PEDOT:PSS, ITO, and polyethylenimine ethoxylated (PEIE), respectively, to study their interface characteristics using high-resolution XPS spectroscopy. As shown in Figure 4, compared with the 200 nm-thick control sample, the XPS spectra of 3 nm-thick CH₃NH₃PbI₃ with different contacts present clear peak shift and additional peaks of derived adsorbates, confirming the occurrence of interfacial chemical reactions. Briefly speaking, the redox decomposition and ion exchange produce O=CH₂−O, CH₃−O, Mo−I surface bonds and CH₃NH₂, CH₃I, I₂ impurities for the MoO₃ contact; CH₃NH₂, CH₃I, I₂, and PbSO₄ impurities for the PEDOT:PSS contact; CH₃−O, NH₃−O, In−I bonds and CH₃I, I₂, PbO impurities for the ITO contact; CH₃NH₂ and PbO impurities for the PEIE contact. It is worth mentioning that metal oxides exhibit a stronger tendency for the formation of volatile adsorbates than organic compounds because of potential catalytic reactions. The electrochemical reaction induced compositional changes are limited to the near-interface region, as reflected by the fact that no change was detected in the XPS spectra of the 200 nm-thick CH₃NH₃PbI₃ sample. Nevertheless, it is a consensus that the defects at contact interfaces can act as trap centers, which hinder the carrier transport and device reliability.

ITO is the most common conductive metal oxide electrode used in perovskite devices. Compared with metal electrodes, ITO/perovskite interface is relatively stable. However, detailed XPS and electrical studies disclosed that thermal stimuli or electrical biasing >1.2 V could activate the perovskite etching of the ITO surface. Moreover, the ITO surface etching can be exaggerated by defects produced by O₂-plasma, which is a typical process for substrate surface cleaning. The electrochemical reactions can generate interfacial trap states and mobile ions, which further deteriorates the ITO contact and perovskite properties. Furthermore, ITO has large energy level mismatch with common perovskite materials, leading to the formation of Schottky barriers and inducing carrier recombination and scattering loss. Similarly, direct contact between fluorine doped tin oxide (FTO) and perovskites could lead to reactive defects and significant interfacial charge recombination. Since metal oxide electrodes are ubiquitous in a wide range of applications due to their transparency, exploiting suitable interfacial engineering is necessary to achieve reliable perovskite contacts.
 Ionic migration is a unique aspect of a wide range of halide perovskites, and it can lead to hysteresis effects in perovskite electronics depending on the type and quantity of mobile ions.[106] Consequently, the performance of device may vary with synthesis details and measurement history, leading to serious reproducibility and stability issues. In MAPbI₃ perovskite, MA⁺, Pb²⁺, I⁻, and hydrogen-derived impurities (H⁺, H₀, and H⁻) are ions that have high mobility and can produce unwanted chemical reactions and hysteresis. Eames et al. surveyed the ionic migration in MAPbI₃ using first-principles computational analyses, yielding the activation energies of Pb²⁺, MA⁺, and I⁻ to be 2.31, 0.84, and 0.58 eV, respectively.[107] The smaller activation energy of I⁻ ions makes them easier to move along the PbI₆ octahedron edges (Figure 5a,b), thus taking the foremost responsibility for hysteresis. The ionic migration behavior can be considerably suppressed by improving the crystallinity of perovskite samples, which has motivated the usage of perovskite single crystals. For example, inverse temperature crystallization has been widely applied to synthesize single-crystalline MAPbBr₃ and MAPbI₃ thin films, which helps minimize trapping defects and restrain ionic migration. [108–111] However, even for single-crystalline perovskites, the electrochemical reaction and interfacial dipole moments at contact interfaces in electronic devices can still result in the ubiquitous formation of mobile ions and the degradation of device performance.

To investigate the electrochemical reaction at contact interface and to disclose intrinsic carrier transport properties, Wang et al. exploited an antisolvent vapor-assisted crystallization process to prepare high-quality single-crystalline MAPbBr₃ and MAPbI₃ thin films, which helps minimize trapping defects and restrain ionic migration.[112] Aiming to create a defect-free interface, the Au contact was prepared using a soft-contact lamination method that avoids surface damages and metal diffusion into the perovskite.[113] Although the lamination method is more gentle than the conventional evaporation or sputtering, both MAPbBr₃ and MAPbI₃ devices exhibit severe I⁻-V hysteresis under electrical bias, implying the appearance of ionic migration and chemical interaction at the perovskite/Au interfaces.[112,114] Interestingly, the hysteresis of MAPbBr₃ device is more pronounced, which can be attributed to the lower activation energy of Br⁻ (0.45 eV) than I⁻ (0.58 eV).[107,112] XPS measurement was carried out on the MAPbBr₃/Au contact area, and as shown in Figure 5e, the observation of AuBrₓ confirms the strong electrochemical reaction at the contact interface.

| Carbon 1s | Nitrogen 1s | Iodine 3d₅/₂ | Lead 4f₇/₂ |
|----------|-------------|---------------|------------|
| P        | CH₃NH₃PbI₁ | CH₃NH₃PbI₁    | CH₃NH₃PbI₁ |
| E        | CH₃NHJ     | CH₃NHJ        | CH₃NHJ     |
| D        | CH₃H₂CH₂J  | NH₃, CH₃NHJ   | CH₃J, In-I |
| S        | O=CH₂O     | O=CH₂O        | Mo₄+, In-I  |

Figure 4. A,b) XPS spectra of CH₃NH₃PbI₃ thin films with thicknesses of 3 nm (a) and 200 nm (b) upon MoO₃, PEDOT:PSS, ITO, and PEIE contacts. The table above indicates the possible interfacial reactions marked by products (P), educts (E), decomposition products (D), and surface bonds (S) in C-1s, N-1s, I-3d₅/₂, and Pb-4f₇/₂ binding energy regions. Table (top) and (a,b): Reproduced under the terms of the CC-BY Creative Commons Attribution 4.0 International license (https://creativecommons.org/licenses/by/4.0).[97] Copyright 2017, The Authors, published by Springer Nature.
The interfacial reaction induced charge redistribution would produce band bending in the vicinity of perovskite surface that promotes ion migration and accumulation. Time-of-flight secondary ion mass spectroscopy was employed to further investigate the interfacial reaction. Under electrical bias, the Br\(^{-}\) ions tend to oxide Au anode to AuBr\(_3\), which is adsorbed at the perovskite surface. In addition, the electrochemical interaction is confined to the interface region with a depth of <100 nm.

In addition to the single-crystalline thin film, millimeter-sized MAPbBr\(_3\) single crystals have been studied regarding their contact with Au electrodes. \[115\] The impedance spectroscopy measurement reveals that Au is able to generate strong polarization at the contact interface to facilitate the migration of Br\(^{-}\) ions, leading to pronounced hysteresis in perovskite devices. \[115\] Even for the fresh MAPbBr\(_3\)/Au interface, the capacitance–frequency plot shows a rapid increase of capacitance at low frequency confirming the interfacial charge accumulation, and the formation of Helmholtz ionic double layer was also observed as illustrated in Figure 5f. \[116\] Surface ionic double layer usually appears when the interface shows liquid-like characteristics. It has been reported previously that the strong electrical field at the interface can urge perovskite to act like a liquid. \[117,118\] When a fierce redox reaction occurs at perovskite/electrode interface, the created field may ionize the surface to form ionic double layer, resulting in the promotion of ionic migration as well as the hysteresis effect.

Intriguingly, contact-induced ionic migration can be beneficial for certain applications such as resistive switching memory. \[119\] For instance, active Ag contact can interact with I\(^{-}\) ions in the perovskite and produce AgI\(_x\) and iodine vacancies (V\(_{I^+}\)). \[120,121\] Because V\(_{I^+}\) tends to migrate under electrical bias, the formation and rupture of V\(_{I^+}\) conductive filaments can be controlled using judiciously tailored set and reset voltages (Figure 5g), leading to resistive switching devices with good performance (Figure 5h). However, for most electronic devices, ionic migration is problematic and leads to inconsistent performance and instability. Mobile defects and contact-induced ionization are two main factors triggering ionic migration. For mobile defects, enhanced crystalline growth, \[110\] grain boundary passivation, \[122\] compositional engineering, \[123\] and electrostatic fixing \[65\] have been studied to suppress ionic transport in perovskite devices. To further mitigate interface-induced ionic migration, constructing an electrical contact with minimized local polarization and alleviated interfacial reaction is the most pressing task in robust and reliable perovskite electronics, which is the focus of this review.

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**Figure 5.** Ionic migration in halide perovskites. a) Perovskite cubic lattice. b) Ionic migration in MAPbI\(_3\) perovskite: I\(^{-}\) ions migrate along the octahedron edge; Pb\(^{2+}\) ions migrate along the diagonal orientation; MA\(^{+}\) ions migrate to the vacancy along the unit cell face. a,b) Reproduced under the terms of the CC-BY Creative Commons Attribution 4.0 International license (https://creativecommons.org/licenses/by/4.0/). \[107\] Copyright 2015, The Authors, published by Springer Nature. c) High-quality single-crystalline perovskites without grain boundary can restrain trapping defects and ionic migration in the crystals. Reproduced with permission. \[108\] Copyright 2015, Wiley-VCH. d) Defect density of perovskite as the grain size increases from 0.1 µm (polycrystalline) to mm scale (single-crystalline). \(N_{gb}\) is the grain boundary defect density. Reproduced with permission. \[111\] Copyright 2018, Elsevier. e) XPS spectrum of MAPbBr\(_3\)/Au reveals the binding energy peaks of Au\(^{+}\) as a result of AuBr\(_3\) formation. Reproduced with permission. \[112\] Copyright 2019, Wiley-VCH. f) Capacitance associated with the MAPbBr\(_3\)/Au interface dramatically increases at low frequency, indicating the accumulation of ionic carriers, as well as, strong interfacial polarization. Reproduced with permission. \[116\] Copyright 2019, AIP Publishing. g) Formation of AgI\(_x\) and V\(_{I^+}\) can generate conductive filaments in the metal-iodide perovskite layer under an electrical bias. Reproduced with permission. \[120\] Copyright 2020, Wiley-VCH. h) Resistive switching of MAPbI\(_3\) perovskite. Reproduced with permission. \[121\] Copyright 2017, Wiley-VCH.
2.3. Energy Level Alignment at Perovskite/Contact Interfaces

Contacting Perovskite not only alters the property near the interface region but also produces a far-reaching impact on the electronic level alignment of the entire perovskite thin film or crystal. In this section, we will discuss two important contact-related effects: energy level alignment in the vicinity of contact and Fermi level offset in the bulk perovskite.

In semiconductor electronics, energy level alignment at contact plays a crucial role in enabling diverse functionalities. Ohmic interface is favorable due to the capability of superior carrier injection and extraction without scattering loss.[124] Energy levels of different perovskites and electrode materials can be seen in Figure 1. In principle, the electrode-semiconductor interface can constitute ohmic upon suitable energy level alignment (Figure 6a,b), namely, $\Phi_m < \Phi_s$ for n-type semiconductor and $\Phi_m > \Phi_s$ for p-type semiconductor, where $\Phi_m$ and $\Phi_s$ are work function (WF) of electrode and semiconductor, respectively.[35] Under these circumstances, the barrier for carrier transmission across the contact interface is small and can be easily overcome by a small bias.

However, the high reactivity and instability of perovskite interface make the story more complicated. Even when the electrode-perovskite energetic configuration satisfies the ohmic alignment, the potential electrochemical reaction may amend the transport property upon the formation of interface. As a consequence, studies on the electronic level alignment reported discrepancies owing to the differences in material preparation and interfacial chemical processes.[74] Many factors can impact the interaction of electrodes with highly reactive perovskites, including air exposure, thermal activation, light illumination, electrical bias, magnetic field, contact material chemistry, and so on. For example, moisture and oxygen tend to capture the electrons from the perovskite layer, leading to p-doping at the junction interface.[124–126] Furthermore, extensive exposure to moisture and oxygen may ultimately decompose perovskite interface and irreversibly destroy the device.[127,128] Similarly, the contact alignment can be undermined by thermal process.[129] As revealed by in situ synchrotron XRD analysis in Kim et al.'s report, under heating at 80 °C, the MAPbI₃ perovskite tends to decompose progressively from the interface to the bulk region while producing by-products of PbI₂, NH₃, and CH₃I.[130] The interfacial reaction can also be triggered by light and electromagnetic field or spontaneously occur when contacting polar materials. Specifically, redox reactions induce charged impurities and defect states, which would alter the Fermi level to produce band bending and ultimately influence the interface property. When perovskite acts as a donor (Lewis base), the upward surface band bending is formed, while the downward bending happens for perovskite acceptor (Lewis acid).[131] Precipitous surface band bending would generate a strong local field that accelerates ions accumulation and hysteresis, thus harming the device characteristics.[132] Hence, the utilization of contact engineering preventing the interfacial reaction is a prerequisite.

![Figure 6. a,b) Ohmic interface energy alignment for n-type (a) and p-type (b) semiconductors. $E_{\text{vac}}$ is vacuum level. $E_C$ and $E_V$ represent conduction band and valence band. $E_{\Phi_m}$ and $E_{\Phi_s}$ are Fermi levels of electrode and semiconductor, respectively. $\Phi_m$ and $\Phi_s$ are WF of electrode and semiconductor, respectively. $\chi_s$ and $E_g$ represent electron affinity and bandgap of semiconductor.](image-url)
for realizing high performance and reliable electronic applications with perovskite materials. For example, ultrathin contact interlayers such as, poly(methyl methacrylate) (PMMA)\cite{133} and SAMs\cite{134} have shown great promise to prevent interfacial chemical reactions, which we will discuss in detail in a later section.

Besides surface band bending, contact-induced Fermi level offset was also observed in bulk perovskites.\cite{135,136} Some researchers call this phenomenon remote doping due to the spatial separation of Fermi level offset from dopants.\cite{73,137} Previous reports have pointed out that the interfacial reaction only occurs near the perovskite contact surface with a depth of <100 nm.\cite{97,112} However, a study on electronic level alignment showed that contact-induced energy level offset could be mostly preserved throughout the perovskite thin film at least for a thickness of 400 nm, which is far beyond the interfacial reaction region.\cite{135} The modification of Fermi energy position is gradually propagated from the contact interface. As an example, XPS and UPS have been used to study MAPbI$_3$ thin film contacted with p-type PEDOT:PSS.\cite{97} The XPS spectra of MAPbI$_3$ at different depths from the interface suggest the range of interfacial reaction is only ≈3 nm, while the UPS measurement illustrates the rearrangement of Fermi level throughout the 200 nm-thick MAPbI$_3$ layer. The energetic band alignment for the MAPbI$_3$/PEDOT:PSS junction is shown in **Figure 7a**. The doping level gradually shifts within the whole MAPbI$_3$ layer as a result of charge redistribution. The pure MAPbI$_3$ thin film after annealing treatment features inherently n-type, and its Fermi level is close to the conduction band as reported by several papers.\cite{138-140} Upon p-type PEDOT:PSS contact, the charge rearrangement shifts the Fermi level to the midgap position near the contact interface while a slight n-type character is found in the opposite edge, indicating that the effect of doping weakens with distance. This phenomenon in perovskites is similar to OSC electronics, in which the WF of the contact material can effectively tune the electronic band of the channel layer via

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**Figure 7.** Electronic level realigned of perovskites with p- and n-contacts. a) Energetic alignment between MAPbI$_3$ and p-type PEDOT:PSS. The interfacial reaction region is shaded, and the band bending region is marked in gray. Reproduced under the terms of the CC-BY Creative Commons Attribution 4.0 International license (https://creativecommons.org/licenses/by/4.0).\cite{97} Copyright 2017, The Authors, published by Springer Nature. b) UPS and IPES data measured on MAPbI$_3$ in contact with p-type NiO$_x$ and n-type TiO$_2$. Reproduced with permission.\cite{135} Copyright 2015, Wiley-VCH. c) Electronic level offset of MAPbI$_3$ with p- and n-type contacts. Reproduced with permission.\cite{136} Copyright 2014, Royal Society of Chemistry.
vacuum level alignment. However, the detailed theory on long-range doping in perovskite still waits to be developed.

It is worth noting that the utilization of p- or n-type contacts could lead to different doping effects in perovskite. Schulz et al. have investigated the electronic band of MAPbI$_3$ contacted with p-type NiO$_x$ and n-type TiO$_2$, respectively. While the powder XRD, atomic force microscopy (AFM), and photoluminescence (PL) experiments reveal exactly the same appearance and emission characteristic for the MAPbI$_3$ samples with different contacts, the UPS and IPES show varied band structures and doping properties, as shown in Figure 7b. Compared with the MAPbI$_3$/TiO$_2$ counterpart, the UPS/IPES spectra of MAPbI$_3$/NiO$_x$ sample demonstrate an increase of WF by 0.7 eV, a decrease of valance band by 0.6 eV, and a 0.7 eV offset of conduction band away from the Fermi level. In other words, the perovskites are slightly p-type and heavily n-type for NiO$_x$ and TiO$_2$ contacts, respectively. A summary of MAPbI$_3$ band offset with p- and n-contacts is shown in Figure 7c. Because of the intrinsically n-type property of MAPbI$_3$, the Fermi level is adjusted to nearly conduction band edge with n-contact, while the p-contact tends to tune the Fermi level to midgap position. Additionally, p-contact produces a much wider interface band bending than n-contact. It is reported that the band bending region in MAPbI$_3$ is from 30 to 100 nm for n-type ITO and PEIE contacts and >200 nm for p-type PEDOT:PSS and MoO$_3$ contacts. The understanding of contact-induced doping can help the design of efficient interfacial energy alignment in perovskite electronics. As an example, Noel et al. spin-coated a thin Mo(tfd-COCF$_3$)$_3$ modification layer on FA$_{0.85}$MA$_{0.15}$PbI$_3$ for p-doping and successfully shifted the WF of perovskite for optimal band alignment.

In the following sections, we will discuss potential electrode engineering strategies to address the crucial issues, such as, interfacial reaction, ohmic interface, and hysteresis, which provide insight for improving the performance of perovskite electronics. Halide perovskites with different A-site cations (MA, FA, Cs, and multi A-site cations) will be discussed together because they possess similar interfacial reactivity tendencies. Despite that the Cs cation is a bit stable than organic MA and FA and multi cations perovskide would slightly reduce ion migration, all these perovskites can react with contact electrodes and have hysteresis issues, and the discussed contact strategies are generally applicable for different composition perovskites.

3. Formation of Ohmic Contact

Up to date, forming a good contact with perovskite is still problematic because of the ubiquitous occurrence of electrochemical reaction, ionic migration, and energy level offset, as aforementioned. For electronic devices, the development of low-resistance ohmic interfaces between active materials and contact electrodes is imperative. Failure to construct good contact may cause significant interfacial scattering loss, as well as, the degradation of device performance. The ionic nature and the soft lattice of perovskites make contact engineering challenging, and several studies have been carried out to probe the hidden perovskite/contact interfaces. In the photovoltaic field, ETLS and HTLS with suitable energy band alignment to obtain effective extraction of charge carriers from perovskite absorbers have been intensively explored to pursue state-of-the-art PSC devices. However, the construction of desirable ohmic contact between electrodes and perovskites for electronics is still an unsolved issue.

Let's start with metal contacts, which are the most prevalent electrodes for perovskite devices. It is perplexing that some reports indicate the observation of ohmic I–V behavior for perovskite/Au interfaces, while the others obtain a Schottky barrier at presumably the same interface. For example, Au/MAPbI$_3$/Au photodetector has been reported with a linear I–V characteristic, indicating the ohmic charge transfer at the two MAPbI$_3$/Au interfaces. On the other hand, Lin et al. reported a Schottky diode behavior of Au/MAPbI$_3$/Au with a barrier height of ~0.2 eV. The contrary interface properties are believed as a result of different preparation methods of MAPbI$_3$ and Au electrodes, which may cause different levels of interfacial reactions. A similar phenomenon was also found for MAPbBr$_3$/Au, where both ohmic and Schottky types were reported in the literature. In other cases, MAPbBr$_3$/Cr and CsPbBr$_3$/Au ohmic junctions have been demonstrated for the application of fast photodetection and field-effect transistor (FET). Thus, even for simple metal contacts, they
may render ohmic behavior once the energy levels are matched and the interfacial reactions and defects are minimized through high-quality growth of perovskite layers and delicate deposition of metal electrodes (Figure 8a–c). Interestingly, it is found that in some cases, the perovskite contact interfaces can be ohmic even when the energy bands are misaligned. It is well known that a vast number of mobile ions and vacancies exist in polycrystalline perovskite films. [107] Zhao et al. found that under an electric field, the mobile ions can accumulate at the perovskite interface and lead to apparent surface band bending. [160] The charge redistribution at the interface is able to reduce the Schottky barrier height, thereby leading to ohmic carrier transport. As a result, either electron or hole injection can be achieved at the same electrode contact depending on the property of the accumulated charges and the surface band bending, as illustrated in Figure 8d. [160]

However, the abovementioned ohmic interfaces are not reliable since the low-resistance charge transfer is highly dependent on the quality of perovskites, the preparation of electrodes, and the elusive ion accumulation. These features make it difficult to forecast the contact property of perovskite devices, and the device performance may vary from one batch to the other. Moreover, even with high-quality perovskite and metal electrodes, it is difficult to retain the ohmic property under external stimuli such as, light illumination, electrical bias, or gas atmosphere, which may trigger chemical reactions at the contact interface. In the following sections, we will discuss potential strategies for achieving reliable perovskite ohmic contacts, including additive modification of perovskites and the implementation of carbon-based electrodes.

3.1. Additives Engineering for Ohmic Interface

Embedding additives to modify electronics properties can be an effective scheme to achieve low-scattering perovskite contacts via the meticulous adjustment of electronic band alignment and the enhancement of perovskite stability. There are two types of additives engineering strategies: additives treatment of perovskite surface and additives doping into perovskite. Perovskite surface treatment by appropriate additives can effectively reduce the density of defects and passivate the grain boundaries, leading to more stable interfaces with contact electrodes. Various kinds of additives have shown potential to improve perovskite surface properties, such as, organic halide salts, inorganic salts, and acids, etc. In the work by Li et al., lead acetate (PbAc$_2$) salts were used to passivate the MAPbI$_3$ and obtain high-quality perovskite with suppressed surface defects. [161] By combining with a dry-transfer contact technique, a desirable MAPbI$_3$/Au ohmic interface was achieved, and the MSM perovskite photodetector features a high detectivity of $1.2 \times 10^{14}$ cm Hz$^{1/2}$ W$^{-1}$. Furthermore, additives surface passivation provides a valuable opportunity for tuning the interfacial energy alignment toward efficient charge injection. For example, Chavan et al. introduced guanidinium iodide treatment on Cs$_x$FA$_{1-x}$PbI$_3$ surface to promote the interfacial charge transfer, in which the
formation of δ-FAPbI₃ phase at the perovskite surface substantially improves the contact band alignment.\[162\] In another work by Cho et al., FABr was applied on a MA₀.₁₅FA₀.₈₅PbBr₀.₄₅I₂.₅₅ film to generate a thin mixed-halide FAPbBr₃₋ₓIₓ layer on the surface.\[163\] This scheme allows fine-tuning of halide ratio at the perovskite surface by adjusting the additive concentration, which has the potential to optimize the band alignment for desirable ohmic contact. Recently, mixed-salt strategies have received increasing attention for perovskite surface optimization since the synergistic effects can provide effective regulation of the perovskite surface properties.\[164,165\] As an example, Suo and co-workers reported the adoption of FABr coupled with different F-substituted alkyl lengths of ammonium iodide on Cs₀.₀₅MA₀.₁FA₀.₈₅PbI₂.₉Br₀.₁ · ₀.₀₅PbI₂ surface, in which the FABr forms an ultrathin FAPbIₓBr₃₋ₓ surface layer to fine tune the energy alignment while the ammonium iodide passivates the surface defects and grain boundaries, leading to a preferred surface morphology.\[165\]

Surface engineering by suitable additives can also create so-called low-dimensional/three-dimensional (3D) perovskite heterostructures, which have been demonstrated to improve the performance of perovskite devices. Low-dimensional perovskite thin layers on 3D perovskites can benefit the contact property because they possess much better stability with reduced ion migration and provide additional opportunities for improving interface energy alignment. To control the interfacial property, Kim et al. applied butylammonium (BA) iodide, octylammonium (OA) iodide, and dodecylammonium (DA) iodide on MA₀.₀₅FA₀.₉₅PbBr₀.₁₅I₂.₈₅ to construct 2D/3D perovskite structures.\[166\] When the length of alkyl groups increases from BA, OA, to DA, the bandgap of 2D perovskite surface layer increases accordingly, showing the potential to adjust interfacial band structure for achieving a desirable contact. Further studies demonstrated that after interfacial treatments, the stabilities of perovskite devices were significantly improved under different humidity and temperature conditions, which was attributed to reduced interfacial reactions due to contact engineering. In another pioneering work, Tong et al. introduced a physical vapor deposition method to fine-tune the excess of PbBr₂ in CsPbBr₃ and produced a dual-phase CsPb₂Br₅–CsPbBr₃ (2D–3D) perovskite thin film.\[167\] It was found that the abundant Br⁻ ions at the film surface can form wide-bandgap CsPb₂Br₅ to improve charge transfer and reduce interfacial decomposition (Figure 9a).\[168\] Consequently, the CsPb₂Br₅–CsPbBr₃ device revealed a linear I–V characteristic with Au contact, as shown in Figure 9b, and the ohmic charge transfer could be retained for more than 65 days in air with a relative humidity of >50%, showing remarkable interfacial stability. The reduction of interfacial reactivity can be attributed to the rich concentration of PbBr₂ at the surface, which can passivate the perovskite by reducing the trapping centers\[169\] and lowering the surface free energy,\[170\] which prevents the perovskite decomposition.

Additives doping is a hot topic in perovskite research, which has been demonstrated to improve perovskite crystallinity and to form dense and smooth perovskite thin films. The mobile ions, vacancies, and lattice strain are the origin of perovskite

![Figure 9. Strategies of embedding additives into perovskite and using carbon-based electrodes to form ohmic contact. a) The excess of PbBr₂ in CsPbBr₃ can form dual-phase CsPbBr₅–CsPbBr₃ perovskite. Reproduced under the terms of the CC-BY Creative Commons Attribution 4.0 International license (https://creativecommons.org/licenses/by/4.0/). Copyright 2020, The Authors, published by Springer Nature. b) Ohmic I–V characteristic of CsPbBr₃–CsPb₂Br₅/Au photodetector. Reproduced with permission.\[167\] Copyright 2018, Wiley-VCH. c) Graphene and CNT are promising candidates for preparing good contacts. Reproduced with permission.\[178\] Copyright 2013, Mineralogical Society of America. d) Ohmic I–V characteristic of a MAPbBr₃/graphene photodetector. Reproduced with permission.\[185\] Copyright 2017, Wiley-VCH.](image-url)
instability. Density-functional theory studies have shown that the implementation of additive dopants with suitable molecular size and binding can effectively passivate the ionic defects and relieve the lattice strain.\cite{171,172} These processes help generate stable perovskite/electrode interfaces due to the lowering of surface free energy by additive dopants. Moreover, doping engineering can modify the electronic band structure of perovskites and even change the majority carriers (equivalently, tune the Fermi level), which is beneficial for contact energy alignment. As an instance, Shahbazi and co-workers reported that additives doping of 1% AgI unexpectedly converted the intrinsic n-type MAPbI$_3$ film to p-type, showing substantial Fermi level tuning.\cite{173} Another work embedded PbS quantum dots (QDs) into MAPbI$_3$ perovskite (weight ratio 2:30) for photodetector applications.\cite{174} The PbS QD additions were found to downshift the conduction band of perovskite, which reduces the junction barrier and forms ohmic transport with Al electrode. Recently, our group added 4% PbS QDs to a MAPbBr$_3$ single crystal and investigated the transport property.\cite{175} Due to the small lattice mismatch, PbS can form epitaxial interfaces with MAPbBr$_3$ and anchor the perovskite atoms to the QD surfaces, thus enhancing the ambient lifetime and thermal stability.\cite{176} As a consequence, the PbS QD doped MAPbBr$_3$ perovskite features ohmic interface with Ag contact, while the pure MAPbBr$_3$ control sample exhibits Schottky characteristic.\cite{175} Additionally, the stability test showed that the pristine MAPbBr$_3$ device was rapidly degraded at 100 $^\circ$C, while the PbS QD doped counterpart maintained consistent performance for 8000 s, indicating remarkably increased stability through additives engineering. For metal oxide electrode contact, Lu and coworkers demonstrated the optimization of ITO/MAPbI$_3$ junction via Cu doping into the perovskite lattice, in which a suitable amount of Cu$^+$ dopants not only suppresses the interfacial charge recombination but also adjusts the Fermi level of perovskite for optimal contact energy alignment.\cite{177} These studies testify that additive engineering is an effective strategy for achieving optimal perovskite contacts via fine-tuning the band structure and alleviating the reactivity of perovskite.

### 3.2. Carbon-Based Ohmic Contact

Carbon-based electrodes have demonstrated an excellent prospect for dependable perovskite contacts (Figure 9c).\cite{178–180} Owing to their desirable physical and chemical properties, including superior electrical conductivity, relatively low cost, large potential window, and most importantly electrochemical inertness, carbon-based electrodes have the potential to minimize interfacial reactions when contacting perovskites.\cite{181} In addition, the hydrophobic nature of carbon can alleviate the penetration of moisture into perovskite, providing an additional bonus to enhance the device stability.\cite{182} Particularly, graphene with remarkable electronic properties has received lots of attention regarding the development of perovskite electrodes.\cite{183–184} Lin et al. have fabricated high-performance nanoscale graphene/MAPbI$_3$/graphene photodetectors featuring an excellent responsivity of 5.6 $\times$ 10$^8$ A W$^{-1}$ and detectivity of 2.8 $\times$ 10$^{16}$ cm Hz$^{1/2}$ W$^{-1}$.\cite{185} The bias-dependent photocurrent presents a good linear relationship, as shown in Figure 9d, denoting the efficient ohmic transport between graphene and MAPbI$_3$. Due to the low-resistance charge extraction, graphene contact has been demonstrated as an ideal platform to study the fundamental properties of perovskite microplates, such as electronic and ionic dual-transport, hysteresis effect, and phase transition.\cite{186} Besides conventional semiconductor fabrication methods, inkjet printing has been applied to fast produce graphene/perovskite/graphene photodetectors with ohmic transport, demonstrating that reliable graphene contacts are available through diverse fabrication techniques.\cite{187}

Thanks to distinct tubular porous structures and outstanding electrical transport properties,\cite{188} carbon nanotubes (CNTs) also showed tremendous potential as an electrode candidate to contact perovskites. Recently, an HTL-free PSC has been demonstrated using CNTs as cathode.\cite{189} The high-quality MAPbI$_3$/CNT interface reveals superior ohmic transport, which eliminates the need for costly HTL in the PSC structure. In addition, the high mechanical resilience of CNTs can provide good support to the active materials for flexible applications. As an example, Veeramalai et al. incorporated CNT bundles with CsPbBr$_3$ nanocrystals to enable the ultraflexible functionality of perovskite photodetectors, and the efficient charge transport between perovskite and CNTs contributes to the high responsivity of 31.77 and 28.79 A W$^{-1}$ under relaxing and bending circumstances, respectively.\cite{189} Overall, the inert electrochemistry of carbon-based electrodes does make them promising candidates for perovskite contact since the interfacial reaction can be reduced and engineers can focus on electronic level alignment to build low barrier ohmic interfaces. In this aspect, the carbon-based electrodes might be superior to metal contact since chemical reactions at perovskite/metal interfaces are almost unavoidable when not using other interfacial engineering techniques.

It should be noted that despite the good compatibility of carbon materials with perovskites, the deposition process of carbon electrodes also plays a decisive role in the contact property. Carbon-based electrodes are normally fabricated using solution processes such as printing and doctor-blading method. In these cases, the solvents in the carbon inks should be orthogonal to perovskites to construct smooth and intimate contacts without degradation. The use of incompatible solvents would damage the perovskite layer and even dissolve it, deteriorating the interface characteristics.\cite{189} Aiming to form a good contact interface, Chu et al. replaced the polar solvent in carbon paste with propylene glycol monomethyl ether acetate, which is an orthogonal solvent for perovskite materials.\cite{192} With this perovskite-friendly carbon paste, the perovskite layer retained dense and uniform morphology, and the contact resistance at electrode/perovskite interface was reduced, showing the importance of solvent selection. Since perovskites are sensitive to processing solvents, dry transfer fabrication is a relatively simple and safe way to construct carbon-based electrodes. Li et al. have demonstrated a soft lamination method to dry transfer CNT electrodes, where the flexible CNT films were conformally coated on the MAPbI$_3$ surface for efficient charge extraction.\cite{193} Since previous works on dry-transferred CNT electrodes have shown promise for use in various applications,\cite{194,195} more efforts are warranted to tailor the process for contacting perovskite materials.
Due to their 2D and ultrathin nature, graphene electrodes may only be suitable for bottom-contact configuration considering that the rough perovskite top-surface may hinder the preparation of high-quality graphene electrodes. It may explain why the most demonstrated perovskite/graphene contacts in literature used the bottom-contact design.[185–187] On the other hand, 1D CNT does not have this limitation, and both bottom-contact and top-contact architectures have been shown effective in previous reports.[189,190,192,193] which may facilitate more applications.

4. Contact Engineering for Reducing Hysteresis

As mentioned previously, hysteresis remains as a bottleneck for perovskite devices as a result of combined effects of mobile ions and trapping defects.[196] Reports suggested that the undesired hysteresis can be partially removed through high-quality crystal growth of perovskites that eliminates grain boundary and bulk recombination centers,[108–110] but the follow-up studies alerted the high correlation of perovskite hysteresis with interfacial contact materials.[112,196] For instance, 2,2′,7,7′-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9′-spirobifluorene (spiro-OMeTAD) and CuI have both been adopted for perovskite hole transport, and a severe hysteresis was obtained for the spiro-OMeTAD contacted device while only a small hysteresis was found for the CuI contacted counterpart.[197] The electrochemical impedance spectroscopy and open-circuit voltage decay studies unveil that the charge carriers are mainly accumulated at the perovskite/spiro-OMeTAD interface and generate a strong interfacial polarization, leading to obvious hysteresis that degrades device performance and stability. Consequently, the development of favorable contacts with less hysteresis and electrochemical inertness has become an imperative task. Below, we will discuss potential electrode contact strategies to reduce interfacial hysteresis, including perovskite doping, less polarized contact materials, and the implementation of intermixed layers.

4.1. Perovskite Doping Toward Hysteresis-Free Contact Interface

Perovskite doping can not only adjust the perovskite energy level for low barrier contact but also stabilize the perovskite phase to reduce interfacial hysteresis.[172,198] Unlike conventional semiconductors, appropriate doping in perovskite does not generate mid-gap trap states but creates favorable host–guest interfaces that passivate unwanted defects and reduce nonradiative recombination, resulting in lower electrochemical reactivity and stable interfaces (Figure 10a).[199–202] Extrinsic perovskite with PbS QD dopants has been widely exploited for the development of hysteresis-free PSCs and different types of devices.[175,176,204,205] Figure 10b,c, taken from our published work,[175] display a typical case of ameliorated perovskite property via PbS QD doping, where a severe hysteresis is observed for the pure MAPbBr$_3$ device whereas the PbS QD embedded counterpart reveals non-hysteric $I$–$V$ characteristic. The major merit of PbS QD is its capability to generate epitaxial interface with perovskite, which passivates the interface and inhibits ionic migration.[176,204] In addition, the perovskite phase becomes stabilized with adequate doping control, thus reducing interfacial reactivity and assisting contact property at the same time.

KI dopants have exhibited the prosperous potential to alleviate hysteresis within perovskite devices.[205–208] It is reported that by doping 5% KI into FA$_{0.85}$MA$_{0.15}$Pb$_{1.25}$Br$_{0.45}$ perovskite, the grain boundaries and trapping defects were diminished, which boosts the carrier lifetime significantly.[203] Most importantly, the $I$–$V$ hysteresis factor was reduced from 0.13 to 0.025 compared with undoped perovskite, illustrating the effectiveness of hysteresis suppression of KI doping (Figure 10d).[205] The passivation dynamic of KI doping was investigated by ultrafast transient absorption and time-resolved PL experiments.[206] It is found that the light illumination triggers the formation of KBr-like complexes at interfaces, which eliminates the interfacial defects and ionic migration. Furthermore, the KBr complexes stimulate irreversible and homogeneous Br to I substitution, which benefits the preservation of the doped perovskite phase as well as the long-term stability.[206] Interfacial electrochemistry between KI doped perovskite and external contact has been probed by Kim et al.[207] Generally, under an electric field, the accumulated ions in the vicinity of contact interface can form the ionic double layer, which plays a critical role in ionic migration and interfacial hysteresis.[177,178] The impedance and electro-absorption studies unveil that the kinetics for the formation of ionic double layer is significantly subsided with the existence of KI dopants, thus facilitating the development of hysteresis-free contacts (Figure 10e).[207] Son et al. further demonstrated that the incorporation of KI doping could be a universal approach toward non-hysteric perovskite devices.[208] By employing 10 μmol of KI dopants, the hysteresis within MAPbI$_3$, FAPbI$_3$, FA$_{0.85}$MA$_{0.15}$Pb$_{1.25}$Br$_{0.45}$ and FA$_{0.85}$MA$_{0.15}$Cs$_{0.05}$Pb$_{1.2}$Br$_{0.3}$ was nearly removed, indicating the passivation effect is applicable for different kinds of perovskites.

Other dopants, such as Zn,[209] Ln,[210] and Al[211] have also been employed to eliminate hysteresis of perovskite devices. In general, the stability of doped perovskite highly depends on the degree of structural compatibility. For example, the Pb–Pb distance of PbS (5.94 Å) is pretty close to the counterpart of CsPbBr$_3$ (5.85 Å), which assists the formation of epitaxial interface and stable perovskite phase.[176] A study of alkali iodide dopants with different iodide radii (LiI, NaI, KI, RbI, and CsI) shows that the hysteresis elimination of KI is the most effective as a result of suitable K/I radius ratio (0.616) that remarkably fits with the octahedral interstitial sites in the perovskite lattice (Figure 10f).[208] A recent study reveals that Mn doping can substantially inhibit the ionic migration in perovskite and reduce the ionic accumulation at contact interface.[212] Another work also indicates that Br doping into an iodide-based 2D/3D perovskite structure effectively diminishes the interfacial defects to yield a better contact property.[213] The optimal doping concentration for perovskite may vary depending on the dopant type, preparation method, and target application but usually below 10 mol%.[172] In transistor application, Siritunga’s group has studied the effect of Rb doping on Cs$_{0.05}$FA$_{0.7}$MA$_{0.27}$PbI$_3$ perovskite with different doping concentrations. The 5% Rb doped perovskite exhibited the best transistor performance with nearly eliminated hysteresis, and the mobility was increased from 0.3 to 0.8 cm$^2$ V$^{-1}$ s$^{-1}$ as
compared to the undoped version. Our group also investigated the effect of adding CNTs into the channel layers of perovskite transistors. When the concentration increased from 0 to 0.5 mg mL$^{-1}$, the hysteresis of the transfer curve was gradually removed.

4.2. Electrode Selections with Non-Polarized Interface

Since interfacial polarization in the vicinity of contact electrode plays a vital role in hysteresis, a straightforward strategy is looking for contact materials that repel the generation of local polarization (Figure 11a). The interfacial polarization originates mainly from electrochemical interaction between perovskite and contact electrode, which gives rise to the formation of interfacial dipole moment and local electric field. In the presence of interfacial electric field, a considerable amount of mobile ions are accumulated in the vicinity of contact electrode, bringing a range of unfavorable effects, including surface band bending, interfacial hysteresis, nonradiative recombination, and interface decomposition, which are widely reported in PSCs and other perovskite devices. As a typical case, MAPbX$_3$ can act with Au to form positively charged coordination complexes that produce p-doped surface region with strong polarization field. Similarly, Ag as another famous electrode can also produce serious interfacial polarization and band bending when contacted with perovskite but result in n-type doping effect rather than p-type owing to the reaction between Ag and X$^-$ anions. Therefore, discovering alternative electrodes with mild interfacial polarization is an urgent task for the development of extensive perovskite applications.

Cr electrode could be the next rising star for contacting perovskites due to the relative inert electrochemistry at the perovskite/Cr junction interface. As a proof of concept, high-quality MAPbBr$_3$ single crystal with Au and Cr contacts have been studied by Tisdale et al. As shown in Figure 11b,c, MAPbBr$_3$/Au interface features a significant electrical hysteresis, while MAPbBr$_3$/Cr exhibits linear I–V and non-hysteric electronic characteristics under various voltage sweeping rates. In order to understand the interface property, impedance spectroscopy was utilized to examine the MAPbBr$_3$/Cr sample. The capacitance data at low frequency suggest the weak interfacial polarization and the elimination of ion accumulation, leading to the non-hysteric behavior (Figure 11d). The interfacial stability between MAPb$_3$ perovskite and a series of noble and transition metals has been analyzed using first-principles calculations (Figure 11e). With inherently n-type MAPb$_3$, Au, Ag, Cu, and Pd tend to form charged metal complexes with low formation energies. On the other hand, Cr, Ni, Co, and Mo with higher formation energies of metal complexes may generate more stable interfaces with perovskite, showing a
good agreement with the weakly polarized perovskite/Cr interface reported in Tisdale’s study.

However, Cr possesses high resistivity ($1.27 \times 10^{-7} \Omega \text{ m}$), which may simultaneously increase the series resistance of device. In consequence, direct use of pure Cr electrode in HTL-free PSC has shown a poor conversion efficiency of 0.14% (Cr/MAPbI$_3$/TiO$_2$/FTO).

Alternatively, highly conductive Au combined with a thin Cr layer can be a prevalent option toward stable perovskite devices, which prevents the interaction between Au and perovskite (Figure 11f). Recently, PSC using Au/Cr (100 nm/3.5 nm) electrode and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF$_4$) dopants (0.3 mol%) into perovskite has demonstrated incredible high stability of 5200 h (20% degradation). Au/Cr electrode is also successful in the electronic field. The incorporation of Au/Cr (22 nm/3 nm) as source-drain electrodes in perovskite FETs has been reported with hysteresis-free and stable operation, suggesting its bright future as reliable perovskite contact. It is worth noting that Ni, Co, and Mo also have the potential to form less polarized interfaces with perovskite according to the first-principles calculations. Up to date, these metals are rarely studied in the perovskite community, which warrants more research efforts to disclose their compatibility with perovskite devices.

As we mentioned earlier, carbon-based electrodes also possess the capability to form chemically inert interfaces with...
perovskites, which open the door for non-hysteretic contact. Multi-walled CNT (MWCNT) has been introduced as the bridge to connect perovskite active layer and paintable carbon-paste electrode (Figure 11g). The resulting HTL-free PSC reveals a nearly hysteresis-free $J-V$ curve and enhanced stability, implying the superior interface property between carbon electrode and perovskite. Another work using MWCNT electrode directly contacted MAPbI$_3$ for HTL-free PSC also presents negligible hysteresis behavior (Figure 11h). These researches suggest the gentle electrochemical interaction between CNT and perovskite, and therefore, the interfacial polarization can be minimized. However, the reduction of interfacial reaction does not mean all carbon-based electrodes are favorable for perovskite since some other effects such as energy level alignment and contact resistance should be taken into consideration. To understand the interfacial charge-transfer dynamics, Zheng et al. have performed impedance spectroscopy measurements on MAPbI$_3$ perovskites contacted with normal MWCNT, thermal treated MWCNT (T-MWCNT), and boron-doped MWCNT (B-MWCNT) (Figure 11i). It is found that B-MWCNT sample owns smaller charge-transfer resistance (270 $\Omega$) than T-MWCNT (390 $\Omega$) and MWCNT (710 $\Omega$), enabling the higher performance of perovskite device. The improved charge transfer is attributed to the boron doping, which modifies the energy level of MWCNT to align with MAPbI$_3$, leading to the lowering of junction barrier, as well as, efficient charge transport. Overall, with less polarized interfaces, carbon-based electrodes do show a prosperous future for non-hysteretic perovskite contact, and efficient interfacial charge transport can be realized via additional engineering such as doping and thermal annealing to lower the interface resistance.

4.3. Electrode Engineering with Thin Interlayer

The problematic interfacial electrochemical reaction between contact and perovskite makes protective interlayers a necessity for electrode engineering. The implementation of chemically inert interlayers can theoretically prevent the formation of charged interface defects so that the interfacial polarization and hysteresis can be minimized (Figure 12a). In a study on the MAPbBr$_3$/ITO Schottky junction, Guan et al. inserted a phenyl-C$_6$H$_4$-butyric acid methyl ester (PCBM) interlayer at the interface and found a significant decrease in $J-V$ hysteresis (Figure 12b). In another work, Kim et al. spin-coated a PEIE interlayer on diethyl-(12-phosphonododecyl) phosphonate (DPP) doped perovskite before the metal electrode coated a PEIE interlayer on diethyl-(12-phosphonododecyl) phosphonate (DPP) doped perovskite before the metal electrode coating a PEIE interlayer on diethyl-(12-phosphonododecyl) phosphonate (DPP) doped perovskite before the metal electrode. The resulting perovskite FET displays negligible hysteresis and exceptional stability owing to the interlayer passivation and doping effect (Figure 12c). It should be noted that the preferred interlayers are usually very thin, therefore, the efficient charge transport between electrode and perovskite is not hindered. For instance, Han et al. employed a few-nanometer-thick PMMA interlayer between Ag electrode and CsPbI$_3$, and ideal ohmic charge transport was observed. Troughton et al. also proposed a niobium-doped TiO$_2$ (Nb-TiO$_2$) interfacial bilayer with a thickness of $<$10 nm (Figure 12d), which helped to generate a near-perfect ohmic contact, and the performance enhancements in PSC, LED, and transistor were demonstrated. In both examples, the chemically inert thin interlayers prevented the interfacial reactions, leading to much improved stability compared to devices without interlayer engineering.

Noteworthy, the implementation of ultrathin contact interlayer is an important and widespread technique in vertical stacked perovskite resistive switching memories (the device structure can be seen in Figure 2c). This is because in resistive memories, the top contact electrode such as Ag is usually highly reactive with halide perovskite, which impedes the long-term stability of devices. The adoption of ultrathin interlayer such as PMMA between the top electrode and perovskite film can provide several advantages: i) it avoids unwanted electrochemical reactions at perovskite/electrode contact interface; ii) the use of inert interlayer prevents the exposure of perovskite film to atmospheric oxygen and moisture; iii) the interlayer can protect perovskite during top electrode deposition without degradation.

Polymer or soft molecular interlayer can also act as buffer layer to relieve stress in perovskite. Strain in the perovskite lattice stems from thermal expansion mismatch between contact electrode and perovskite during annealing or high-temperature processing. Perovskites have higher thermal expansion coefficients in the range from 3.3 to $8.4 \times 10^{-5}$ $K^{-1}$, while ITO/FTO coated glasses are from $0.37$ to $1 \times 10^{-5}$ $K^{-1}$ and typical metal electrodes are from 0.6 to $2.4 \times 10^{-5}$ $K^{-1}$. Besides lowering the processing temperature, using a soft buffer interlayer can release the interfacial strain and improve the contact property. For example, Wu et al. have verified that polystyrene buffer interlayer can effectively reduce lattice stress in perovskite, improving the device performance.

Among the various types of interlayer engineering, SAMs have received increasing attention for their use in perovskite contact due to their high-quality and uniform interface and ultrathin nature. For ultrathin inert interlayer like hydrophobic PMMA, the molecular interaction between perovskite and interlayer is weak. In contrast, SAMs feature strong binding such as hydrogen bond anchoring to the interface, which not only prevents the reaction between perovskite and electrode materials but also plays a more positive role in modifying the interface property. Sirringhaus’s group has examined different materials as metal electrode intermixed layers to improve perovskite transistor contact, including conventional conductive buffer layers (MoO$_3$ and PEDOT:PSS) and SAMs (PEIE and perfluorobenzenethiol (PFBT)). With conventional interlayer, the FET performance is marginally enhanced, but the best performance is observed based on SAMs. By inserting PFBT-SAM between Au electrode and MAPbBr$_3$, the hysteresis is significantly reduced, as shown in Figure 12e,f. Furthermore, the ON/OFF ratio of perovskite FET is largely improved from $10^2$ to $10^6$, demonstrating the superior property of PFBT intermixed monolayer. Due to the capability to subside hysteresis, other SAM materials were also explored for perovskite transistors. Matsushima et al. introduced NH$_4$I–SAM interlayer into 2D (Cs$_2$H$_2$C$_6$H$_4$NH$_3$)$_2$SnI$_4$ perovskite FET resulting in the hole mobility enhancement from 6.4 to 12 cm$^2$ V$^{-1}$ s$^{-1}$ without notable hysteresis (Figure 12g). In our recent work, by using PEIE–SAM contact interlayer and CNT doping into...
perovskite, we demonstrated the minor hysteric FET featuring remarkable hole mobility of 32.2 cm$^2$ V$^{-1}$ s$^{-1}$ and ON/OFF ratio up to $10^7$ (Figure 12h). The XPS measurement shown in Figure 12i reveals that the PEIE interlayer helps prevent the interaction between Au electrode and perovskite, in contrast to the observed interfacial reaction on the sample without PEIE-SAM. Although PEIE is inherently insulating, the ultrathin nature of the interlayer allows efficient charge transfer through thermionic injection and tunneling, leading to excellent contact property. Since SAMs may become a spotlight in future perovskite contact studies, in the next section, we will further discuss the role and multiple functionalities of SAMs, which opens several opportunities for perovskite electronics.

5. Contact Engineering with Self-Assembled Monolayers

SAMs represent a successful technique of interface engineering that exploits organic molecules spontaneously assembled on semiconductor surfaces through solution or gas phase processes. In addition to the capability to reduce interfacial hysteresis we just discussed, SAMs are able to amend the performances of perovskite electronics in a substantial manner via enhancement of interfacial carrier transport, passivation of surface trap states, and modification of perovskite surface morphology and its grain size. Due to these advantages, SAMs have been exploited in PSC architectures to improve the
charge carrier transport across the HTL and ETL, which have been recently reviewed. Here, we focus on the role of SAM between perovskite and electrode contact, which plays a crucial role in perovskite electronics as well as HTL- or ETL-free PSCs.

5.1. Modification of Energy Level Alignment

SAM as a mature interfacial engineering technique has been developed for organic electronic devices to improve the charge transport of electrical contact. Driven by this, the implementation of SAMs into perovskite contact is reasonable due to the organic–inorganic hybrid property and ionic feature of perovskite surface. Inserting SAM interlayer can yield an inter energy level between perovskite and contact electrode, which helps produce interfacial cascade energy alignment, thus benefiting the carrier transport. In addition, the physical property of electrode can be effectively tuned by SAM intermixed layer to achieve desirable electrical conduction. For example, Chang et al. have employed 3-mercaptopropyltrimethoxysilane (MPTMS) SAM to alter the property of Ag electrode. As shown in Figure 14a, the thin Ag film deposited on MPTMS-SAM features a much more homogeneous surface (roughness: 1.4 nm) compared with the control sample (roughness: 4.3 nm). Accordingly, a remarkable reduction in sheet resistance of MPTMS modified Ag film is observed, leading to better performance in electrical conduction (Figure 14b). Furthermore, through the formation of dipole moment at electrode interface, SAMs are able to adjust the WF of electrode to a desirable position, which helps the contact energy alignment as well as the charge-transport property. UPS measurement has been introduced to examine Ag electrode with (11-mercaptoundecyl)trimethylammonium bromide (MUTAB) SAM modification. While the pristine Ag electrode remains the WF of 4.67 eV, the MUTAB assembled version demonstrates a reduction of WF to 3.35 eV, clearly showing the band modification effect of SAM intermixed layer (Figure 14c). The WF of Au electrode can also be modified by SAM. Lin et al. have erected Au/MAPbI₃/Au back contact architecture and decorated the opposite Au electrodes by 4-methoxythiophenol (OMeTP) and 4-chlorothiophenol (CITP) SAMs with different concentrations, respectively. Afterward, a WF difference of 550–580 meV between the Au counter electrodes was obtained using the Kelvin probe force microscopy (KPFM), indicating the WF shift can be precisely controlled with different levels of SAM modification (Figure 14d–i). The J–V scan of SAM-modified back contact device under simulated sunlight shows negligible hysteresis behavior and a VOC of ≈565 mV, which is consistent with KPFM measured WF difference. This observation confirms that the device performance can be controlled using SAMs that tune the WF difference between two contacts. Additionally, by managing the orientation of interfacial dipole moment of SAM, both increase and decrease in electrode WF can be realized. For instance, it is reported that using PFBT SAM, the WF of Au is adjusted from 5.2 to 5.4 eV, while PEIE modified Au features a WF shift down to 4.5 eV (Figure 14j).

Specifically, the metal WF tends to decrease when the anions of SAM assemble to the metal surface and cations are distributed above, while it increases in the case of cation anchoring. In Wang et al.’s work, the improved electrode/perovskite energy alignments were reported using carbolong-derived complexes electrode interlayers, whose [BF₄]⁻ and [OTF]⁻ anions can anchor to metal surface and decrease the metal WF, such as, Au or Ag, due to interfacial dipoles. FTO as a famous metal oxide electrode was also modified using SAM engineering in order to efficiently extract charge carriers from perovskite. An UPS study reveals that when the thickness of PEIE intermixed layer gradually increases from 0 to 10.8 nm, the WF of FTO...
electrode reduces from 4.02 to 3.65 eV simultaneously, showing the fine control of energy level modification (Figure 14k,l). Al-Ashouri et al. also demonstrated the improved contact property between ITO electrode and perovskite utilizing carbazole bodies based SAM interlayers such as [2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid and [2-(9H-carbazol-9-yl)ethyl]phosphonic acid. The reported SAMs with phosphonic acid anchoring groups provide desirable energy levels well-aligned with perovskite, and the PL transient study evidences the absence of non-radiative losses at the contact interface. Through the fine-tuning of electrode WF, the realization of ohmic transport at electrode/perovskite interface is also possible. In Huang et al.’s work, 4,4′-([(methyl(4-sulfonatobutyl)ammonio)bis(propane-3,1-diyl)]bis(dimethyl ammoniumdiyl)]bis-(butane-1-sulfonate) (MSAPBS) nonconjugated small-molecules was spin-coated on ITO electrode to modify its energy level. The interfacial dipole moment correspondingly lowered the WF of ITO electrode, and a desirable ohmic contact is achieved between the MAPbI3 and the molecule-modified electrode. Overall, the ease of interface modification and simple fabrication process of SAMs suggest a promising way to control the energy alignment and charge transport across the junction barrier, which allows us to pursue optimization of electronic performances for perovskite devices.

![Figure 14. SAM engineering for tuning electrode property.](image-url)
5.2. Passivation Effect

Another important function that SAMs offer is perovskite passivation. SAM molecules with compatible surface functional groups are able to coordinate with the ionic vacancies in perovskite surface to create strong bonding and passivate the interface states. This approach is also known as Lewis acid–base interaction, which has been developed for semiconductor surface passivation.[244] For example, Li et al. have introduced butylphosphonic acid 4-ammonium chloride (4-ABPACl) to modify MAPbI$_3$ perovskite surface.[245] The nuclear magnetic resonance measurement indicates that the phosphonic acid group can interact with halide anion (act as Lewis base) in the PbI$_4^{2-}$ framework to produce hydrogen bonding that passivates perovskite surface (Figure 15a). In another example, iodopen-tafluorobenzene (IPFB) SAM was exploited on MAPbI$_3$Cl$_x$ perovskite thin film for surface passivation, in which the IPFB (Lewis acid) can bind with surface halide anion (Lewis base) to form supramolecular halogen bonding (Figure 15b).[244] Due to the reduced number of under-coordinated halide anions and trapping defects at the perovskite surface, the nanosecond transient absorption dynamics show a much longer lifetime and inhibited interfacial recombination for the sample with IPFB, thus confirming the role of SAM passivation.

On the other hand, when SAM functions as Lewis base anchoring to perovskite surface, under-coordinated Pb atom plays a major role rather than halide anion. Zu et al. have observed that the reduced Pb$^0$ at perovskite surface acts as donor-like defect, leading to severe Fermi level pinning and surface band bending.[146] UPS and XPS experiments reveal that using acceptor SAMs such as 1,4,5,8,9,12-hexaazaatrichloropentacene-hexacarbonitrile (HATCN) and 2,2′-(perfluoronaphthalene-2,6-diylidenedijimalononitril) (F6TCNNQ) to passivate perovskite surface, Pb$^0$ induced surface band bending is released owing to preferred Lewis acid–base interaction (Figure 15c).[146] Another work applying Lewis bases thiophene and pyridine on MAPbI$_3$Cl$_x$ perovskite surface demonstrates greatly reduced nonradiative recombination and enhanced carrier lifetime by seven times, implying favorable passivation of under-coordinated Pb (Figure 15d).[146]

The anchoring effect provided by SAMs can also impact the surface morphology and crystallinity of perovskites. In a significant case, Senanayak et al. fabricated MAPbI$_3$ thin-film transistors using pristine and SAM modified Au (i.e., PEIE and PFBT, respectively) as source-drain electrodes.[214] The SEM morphology measurement in the channel region indicates the grain size of ≈150 nm for MAPbI$_3$ thin film with bare Au contact and ≈200 nm for the other two specimens with PEIE and PFBT contact interlayers (Figure 15e,f), illustrating the improvement of perovskite crystallinity with SAM modification layers. Larger grain size in perovskite thin film is preferred since defect trap states and scattering centers at grain boundaries are reduced, thus promoting carrier mobility and device performance.[246] In consequence, room temperature mobility of 0.5 and 3 cm$^2$ V$^{-1}$ s$^{-1}$ were measured for transistors with PEIE and PFBT SAMs, whereas the control device with bare Au contact only displayed mobility of 0.02 cm$^2$ V$^{-1}$ s$^{-1}$.[214]

The improved crystallinity can be attributed to contact-induced enhancement of perovskite nucleation, in which the suitable bonding or Lewis acid–base interaction provided by SAMs help passivate the grain boundaries and link the adjacent grains. Take PEIE as an example, the abundant amino and imine groups in PEIE tend to be protonated and make the terminal domains positively charged, which can bond with halide ions of perovskite and strengthen the film uniformity and compactness.[245] Under bottom-contact conditions, the implementation of SAMs can also modify the perovskite growth at the contact region, which is similar to the observation in OSC-based electronics.[246–247] Generally, the crystallinity of the resulting thin film highly depends on the affinity of SAM’s terminal group to the perovskite. As an example, Hou et al. demonstrated that MAPbI$_3$ thin film growth on dopamine SAM yields a larger grain size than the control sample without SAM.[246] Due to the suitable hydrogen bonds between amino groups and iodide ions, the MAPbI$_3$ nucleation is strengthened, leading to better crystallization. In another study, Kim and coworkers examined the growth of MAPbBr$_3$ films on pristine and surface modified Au using four different SAMs 4-mercaptopypyridine, 4-aminothiophenol, cysteamine, and thiophenol.[249] A series of microscopy and spectroscopy measurements indicated that the perovskite crystallinity and optical properties are substantially improved by SAMs engineering and the 4-mercaptopypyridine sample presented the best result due to the affinity to the Pb ions.

SAM can not only passivate the surface defects but also act as water-resistant layer to shield underlying perovskite against the moisture in atmosphere. Fullerene linked with trichloro(3,3,3-trifluoropropyl)silane has been assembled on MAPbI$_3$ surface for SAM engineering (Figure 15g).[230] Thanks to the hydrophobic nature of trifluoromethyl functional groups, the SAM interlayer features outstanding water resistance, thus preventing the penetration of moisture into perovskite. The impedance measurement demonstrates one semicircle for the perovskite device with hydrophobic groups and two semicircles for the control sample, which manifests reduced interfacial recombination in the presence of water-resistant SAM. Moreover, the perovskite device with hydrophobic modification exhibits much enhanced ambient stability and non-hysteresis property, suggesting successful interface engineering of SAM.

There are some tips to prepare high-quality SAMs:[232,251,252] i) when the SAM assemblies to perovskite or electrode, the surface should be flat and clean without contamination; ii) if the SAM assemblies to the metal surface, the metal electrode should contain an adhesion layer (such as, Ti or Cr) underneath to avoid delamination; iii) the SAM solvent must be degassed before use and all the assembly process should take place under inert gas (such as, Ar or N$_2$) underneath to avoid delamination; iv) although self-assembly can take place rapidly, longer assembly time of 24–48 h is recommended to improve monolayer packing; v) the time between SAM preparation and deposition of the following layer should be minimized to avoid oxidation over time.

It is worth noting that the top-contact and bottom-contact configurations have different impacts on the perovskite/electrode interfaces. For the top-contact case, the perovskite layer might be damaged during metal deposition. To this end, gentle depositions and soft lamination methods are preferred to create undamaged contacts and to conserve the desired
interface property. Besides, the use of interlayer engineering such as, SAMs can effectively protect the underlying perovskite and minimize potential harms during top electrode deposition. Unlike top-contact circumstances, bottom-contacts usually suffer from solution etching. Perovskites are well known for their compatibility with simple and cost-effective solution processes, however, previous reports indicated that the spin coating of perovskite precursor solution could severely etch the bottom

Figure 15. SAM for perovskite passivation. a) 4-ABPACl SAM can form hydrogen bonds with halide anion to passivates perovskite surface. Reproduced with permission.[242] Copyright 2015, Springer Nature. b) Lewis acid–base interaction between IPFB SAM and halide anion. Reproduced with permission.[243] Copyright 2014, American Chemical Society. c) UPS and XPS spectra of illuminated MAPbI$_3$Cl$_x$ with different thicknesses of 6TCNQ SAM, illustrating the reduction of Pb$^2+$ by SAM passivation. Reproduced with permission.[147] Copyright 2017, American Chemical Society. d) Timeresolved PL of MAPbI$_3$Cl$_x$ perovskites with and without SAM treatment. Reproduced with permission. Copyright 2014, American Chemical Society. e) SEM images and f) grain-size statistics (in channel region) of MAPbI$_3$ transistors using bare and SAMs modified Au as source-drain electrodes. e,f) Reproduced under the terms of the CC-BY Creative Commons Attribution 4.0 International license (https://creativecommons.org/licenses/by/4.0/).[114] Copyright 2017, The Authors, published by American Association for the Advancement of Science (AAAS). The length of yellow scale bars is 200 nm. g) SAM with hydrophobic functional groups for perovskite passivation. Reproduced under the terms of the CC-BY Creative Commons Attribution 4.0 International license (https://creativecommons.org/licenses/by/4.0/).[250] Copyright 2016, The Authors, published by Springer Nature.
metal electrodes. Consequently, the interface engineering is imperative for achieving reliable bottom-contact. In recent advances of perovskite FETs, both PEIE and PFBT SAMs have been demonstrated to effectively protect the bottom electrodes from perovskite solution etching and to optimize the contact properties for high-performance FETs. Overall, due to the merits discussed above, SAMs may represent the most promising contact technique for further development of high-performance perovskite electronics.

6. Conclusion and Outlooks

The high surface reactivity of perovskites brings about a series of intricate electrochemical effects at contact interfaces, which calls for lots of attention from the research community. The interfacial redox reaction triggered by moisture, illumination, electric field, or polar contact materials tends to generate high-density charged impurities and defects, leading to considerable nonradiative recombination and scattering loss in perovskite electronics. Such degradation of device performance cannot be deemed as an intrinsic property of halide perovskites, and it is unwise to sweep it under the carpet in the endeavor of advancing perovskite-based technologies. Even for high-quality and grain-boundary-free perovskite single crystals, interfacial reaction induced electric field or ionic double layer can still produce severe hysteresis, which makes perovskite suffer from reproducibility and stability issues. Furthermore, surface band bending and interface decomposition have been regarded as major roadblocks for achieving the contact energy alignment expected from the conventional wisdom. The discrepancy in perovskite synthesis and interfacial reaction also makes contact characteristics vary among reports from different laboratories. Considering these difficulties, contact engineering to eliminate or at least suppress parasitic interfacial effects is imperative for further advancing perovskite electronics.

Additives doping possesses an immense potential to ultimately settle the high reactivity issue of perovskites and to achieve the optimal contact property. Moreover, with adequate doping control, the energy levels can be adjusted to form beneficial ohmic interface for efficient charge transport. Electrode selection is important for the generation of non-polarized interface. Among metal electrode materials, Cr with high formation energy of metal-halide impurities has been proved as a promising candidate for contacting perovskites. To further reduce the series resistance, Au/Cr electrode is a favorable choice for perovskite electronics. Carbon-based electrodes featuring high conductivity and electrochemical inertness have also been demonstrated for creating non-hysteretic and ohmic interfaces with perovskites. Due to its cost-effective feature, carbon-based electrodes will occupy a pivotal position in future perovskite technologies since the cost is always an important concern in large-scale industry applications.

The use of few-nanometer-thick contact interlayer has shown the capability to prevent interfacial electrochemical reactions for perovskite contact. SAM engineering as a successful technique in OSC electronics appears to be also applicable in the arena of perovskites. The implementation of SAM interlayer brings numerous benefits, including the reduction of interfacial recombination, efficient charge transport, suppressed hysteresis, and passivation effect, leading to optimal contact property and stability. In addition, the capability of SAM to simultaneously tune the perovskite morphology and energy level alignment provides a promising scheme to enhancing electronic performance. Other contacts technique used in OSC electronics may also be useful for improving the perovskite devices. The “soft landing” method such as stamping transfer and soft-contact lamination, which effectively create contacts in an undamaged manner, should be advantageous for perovskite electronics, which warrants more research efforts.

It is worth noting that the aforementioned techniques can be combined to enhance the contact performance in perovskite electronics. In a recent work, Senanayak et al. demonstrated hysteresis-free FETs using multiple contact engineering methods, including Rb dopants in the perovskite lattice, utilization of Au/Cr source-drain electrodes, and SAM interface modification, thereby achieving superior stability and mobility. Additionally, with surface treatments of Lewis base and acid, both n- and p-type operations of transistors were realized.

Another critical factor of perovskite/electrode interface is contact resistance, but it has not yet been thoroughly investigated in perovskite electronics. Only a few papers reported the contact resistance values in perovskite transistor, which warrants more research efforts. Besides electrode contact engineering, the optimization of substrate and gate dielectric should also be pursued to further advance perovskite electronic devices. When growing perovskite layers, the choice of substrates may affect perovskite crystallinity, grain size, and defect formation. For transistor applications, the gate dielectric materials can also produce direct impacts on perovskite channels. In some preliminary studies, the use of high-k and molecule-modified dielectric layers have shown promising potential to improve gate modulation of perovskite transistors.

The perovskite/electrode contact engineering discussed herein can also assist the design of HTL- or ETL-free PSCs and reduce the manufacture costs via eliminating the use of expensive charge-transporting materials. For LED applications, the SAMs technique has potential to replace the existing carrier-injection layers and to make the device fabrication more cost-effective, which can be a promising research direction. Compared with perovskite photovoltaic and LED technologies, the development of perovskite electronics is still in its infancy stage. There remains plenty of room at the perovskite/electrode interfaces for researchers to explore. With growing attention and effort on contact engineering and fundamental understanding of perovskite interfaces, we have ample reasons to believe that the development of versatile perovskite electronics will be greatly accelerated in the near future.

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Conflict of Interest

The authors declare no conflict of interest.
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