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Photovoltaic Diode Effect Induced by Positive Bias Poling of Organic Layer-Mediated Interface in Perovskite Heterostructure α -HC(NH₂)₂PbI₃/TiO₂

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It is shown that in the formamidinium (FA) lead iodide/titania heterostructure α -HC(NH₂)₂PbI₃/TiO₂ the organic layer-mediated interface, i.e., FAI/TiO₂, can induce photovoltaic diode effect via positive bias poling. The band gap of the heterostructure is reduced to zero upon the positive poling due to combined effects of ion diffusion, rotation of organic moieties, and ferroelectric redistribution. The perovskite part in the organic layer-mediated interface FAI/TiO₂ gives rise to a strong polarization of 18.69 μ C cm⁻², compared to that (0.89 μ C cm⁻²) in the inorganic layer-mediated interface PbI₂/TiO₂. The strong polarization of the organic layer-mediated interface is closely related to the diode effect associated with the reordering of the ferroelectric polarization and charge distribution, as a consequence of the mobility and rotation of organic moieties in FAI/TiO₂ upon the positive bias poling. The latter effect also provides an explanation on why the FAPbI₃-based devices can largely reduce the scanning hysteresis in the J-V curves (Yang et al., Science 2015, 348, 1234) and why the organic layer-mediated halide perovskite heterostructure is one of the most promising candidates for the fabrication of highly efficient solar cells or optoelectronic devices.

1. Introduction

Inorganic–organic halide hybrid perovskite solar cell has received enormous research and development interests owing to its low-cost solution-processed synthesis and high power conversion efficiency (PCE).^[1–7] A certified value of 20.1%^[8] has been reached from the original value of 3.8% over a short period.^[2] The hybrid perovskites also have potential application

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in electrically and optically readable memristors and circuits.^[9] Methylammonium lead iodide CH₃NH₃PbI₃ (MAPbI₃) is the prototype inorganic-organic halide hybrid perovskite and possesses a band gap of 1.55 eV,^[4] allowing optical absorption over the whole range of visible light. The band gap can be further reduced to 1.47 eV^[10] by substituting MA with another organic molecule HC(NH₂)₂(FA), extending the absorption spectrum to the infrared (IR) region. The cation in FAPbI₃, i.e., HC(NH₂)₂, has a bigger ionic radius than CH₃NH₃ in MAPbI₃, leading to the reduced band gap and the broad light harvesting in the IR spectrum region.^[8] FAPbI₃ is relatively unstable compared with the MAPbI₃ while the mixed structure, (FAPbI₃)_{1-x}(MAPbBr₃)_x, can be a stable perovskite phase with higher device performance.^[10] The high temperature α phase of FAPbI₃, a black perovskite, exhibits the trigonal structure with the

space group P3m1 which can be changed to the yellow hexagonal nonperovskite phase (δ phase) with space group $P6_3mc$ at an ambient atmosphere.^[4] The trigonal phase possesses a corner-sharing PbI₆ octahedral network while the hexagonal phase exhibits a face-sharing PbI₆ octahedral network, giving different electronic characteristic and device performance. In addition, the phase transition is reversible when the yellow nonperovskite phase is annealed. Recently, high-resolution neutron powder diffraction was used to accurately determine the structure of the black FAPbI₃ at 298 K, and, interestingly, the cubic structure with pm3m space group was obtained.^[11] The black FAPbI₃ is most likely the microdomains of twinned or irregular cubic phases, and it is not necessary to use the bigger trigonal cell to describe the α -FAPbI₃.

To date, the carrier separation and charge transfer at the interface of planar hybrid perovskites/TiO₂ heterojunction has been established as the key mechanism involved in the perovskite solar cells.^[12–16] Although many density functional theory (DFT) studies of the electronic, structural, and optical properties of bulk organohalide perovskites have been reported,^[17–24] limited theoretical studies of the interfacial effect of the perovskite/TiO₂ heterostructure have been published in the literature due in part to the relatively large lattice mismatch between MAPbI₃ and anatase TiO₂. To address this issue in DFT computation, a larger supercell is needed to reduce or remove the in-plane strain

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involved when constructing the heterostructure.^[25,26] Thus far, the MAPbI_{3-x}Cl_x/TiO₂ interface with a large supercell has been optimized based on the numerical pseudoatomic basis (the planewave basis would be computationally very demanding).^[25,26] However, the charge transfer mechanism is still incompletely understood. Previously, we have systematically investigated the charge accumulation at the interface of CH₃NH₃Sn_xPb_{1-x}I₃/TiO₂ heterostructures with ~6% in-plane strain by using DFT and time-dependent DFT (TD-DFT).^[27] We suggest that the charge transfer is related to the built-in field across the interface.^[27]

In this study, the lattice misfit between the cubic FAPbI3 and rutile TiO₂^[28] is merely $\approx 1.9\%$ when using the $a'\sqrt{2} \times b'\sqrt{2} \times c'$ supercell of the cubic FAPbI₃ and the $a'2 \times b'2 \times c'$ supercell of rutile TiO₂ to build the heterostructure. As such, the charge transport in the α -HC(NH₂)₂PbI₃/TiO₂ interface can be studied using the more accurate plane-wave basis. Note that in the current–voltage (J–V) measurements, it has been found that the photocurrent hysteresis, which depends on the voltage scanning direction and rate, can lower the performance of the hybrid perovskite solar devices.^[1] Remarkably, the forward and reverse scanning hysteresis of the *I*-V curves can be largely reduced when the FAPbI3-based devices are adopted.^[8] This interesting behavior is apparently associated with the ionic diffusion and defect mobility upon bias poling on the solar devices.^[9,29,30] The hysteresis in *I-V* measurements upon changing sweep direction and scanning rate is suggested due to the following factors: the ferroelectricity in the perovskite caused by the rotation of the organic moieties and the reorientation of the PbI₆ octahedra upon external electric field; possible charge carrier traps in the interfacial region and the surface of the perovskites; and the ionic diffusion and defect mobility upon bias poling. Recently, several experiments show that the rotation of the organic moieties of the inorganic-organic hybrid perovskites and the charge accumulation appear to be very important to the *I-V* hysteresis,^[31] and that the interfacial structure itself also plays certain role in the current-voltage hysteresis.^[32] All these factors should be investigated theoretically to gain a deeper understanding of the experiments and for better designing perovskites solar cells with more efficient performance. Here, we suggest that the hysteresis is closely related to the ionic mobility and carrier traps in the interface where the ionic diffusion can cause the reorientation of the polarization. Importantly, to simulate the experimental current-voltage sweep, the ionic mobility and charge transfer of the planar perovskite cells upon external electric field should be studied. Based on DFT and TD-DFT computation of α -FAPbI₃/TiO₂ heterostructure, we report a systematic study of the interfacial effect on the charge transport and the interaction with the photogenerated field upon external voltage poling. This study provides an account for the carrier separation and charge transfer in the FAPbI₃/TiO₂-based solar devices that give the highest efficiency.^[8]

2. Computational Methods

We used Quantum ESPRESSO package to perform the DFT and TD-DFT computations.^[33–35] The exchange correlation interactions are described by the Perdew–Burke–Ernzerhof (PBE) parameterization of the generalized gradient approximation



Table 1. Fully relaxed lattice constants for Pbl₂/TiO₂ (a), FAI/TiO₂ (b) interfaces, cubic formamidinium lead iodide, and rutile TiO₂. $a'\sqrt{2} \times b'\sqrt{2} \times c'$ supercell of the α -FAPbl₃ and $a'2 \times b'2 \times c'$ supercell of rutile TiO₂ are used to construct the heterostructures. The lattice misfit between α -FAPbl₃ and rutile TiO₂ is only $\approx 1.9\%$. $a = a'\sqrt{2}$, $b = b'\sqrt{2}$, and c = c'. Exp. and Opt. denote the experimental structures and the fully optimized structures, respectively.

	a [Å]	b [Å]	c [Å]	$\alpha = \beta = \gamma [^{\circ}]$
PbI ₂ /TiO ₂ (Opt.)	9.188	9.188	25.856	90
FAI/TiO ₂ (Opt.)	9.288	9.288	25.856	90
α-FAPbI ₃ (Exp.) ^[11]	8.997	8.997	6.362	90
Rutile-TiO ₂ (Exp.) ^[28]	9.174	9.174	2.954	90
	a´[Å]	b′[Å]	c′[Å]	$\alpha = \beta = \gamma [\circ]$
α-FAPbI ₃ (Exp.) ^[11]	6.362	6.362	6.362	90
Rutile-TiO ₂ (Exp.) ^[28]	4.587	4.587	2.954	90

for solid (PBEsol).^[36] The interactions between valence electrons and ions are described by the GBRV ultrasoft pseudopotential.^[37] $a'\sqrt{2} \times b'\sqrt{2} \times c'$ supercell of the cubic FAPbI₃ and $a'2 \times b'2 \times c'$ supercell of rutile TiO₂ are used to build the interfacial heterostructures. The lattice parameters for bulk FAPbI₃ and TiO₂ are taken from the experimental measurements. We considered two possible interfaces for α -HC(NH₂)₂PbI₃/TiO₂ heterostructure, i.e., PbI2/TiO2 and FAI/TiO2 interfaces. The interfacial structures for both interfaces are fully optimized with lattice constants and atomic positions being relaxed until the forces on the ions are less than 0.001 Ry per a.u. A thickness of about 12 Å of atomic layers is incorporated in the slab model, and the thickness of vacuum is the same level as the atomic layers. The lattice constants for the fully relaxed PbI₂/TiO₂, FAI/ TiO_2 interfaces, bulk FAPbI₃, and TiO_2 are given in Table 1. $8 \times 8 \times 1$ Monkhorst–Pack sampling of the Brillouin zone is used to make sure the convergence in the total energy calculations. TD-DFT calculations are carried out by using the PBE exchange-correlation functional and the double numerical plus polarization basis set, implemented in the Dmol³ package.^[38,39] Spontaneous polarization (P) of the hybrid perovskite part is calculated from the modern theory of polarization.^[40,41] The electronic part of P is calculated from the following formula^[40,41]

$$\mathbf{P}_{el} \bullet \mathbf{b}_{i} = \frac{fe}{\Omega N_{\perp}^{i}} \sum_{l=1}^{N_{\perp}^{i}} \operatorname{Im} \ln \prod_{j=0}^{N_{l}-1} \det S(\mathbf{k}_{j}^{(i)}, \mathbf{k}_{j+1}^{(i)})$$
(1)

where N_{\perp} is the divisions along \mathbf{b}_i . *S* is the overlap integral in the *k*-space as

$$S_{nm}\left(\mathbf{k},\mathbf{k}'\right) = \left\langle u_{nk} \,|\, u_{mk'} \right\rangle \tag{2}$$

where n and m are the occupied bands.

3. Results and Discussion

3.1. Cubic and Trigonal $\alpha\mbox{-}FAPbI_3$ and Interfacial Structures of $FAPbI_3/TiO_2$ Heterostructures

The crystal structures of the cubic and trigonal α -FAPbI₃ are shown in Figure S1 (Supporting Information). The cubic



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phase with pm3m space group looks simpler, while the trigonal one can be seen as the twinned domains of cubic structure. When considering $a'\sqrt{2} \times b'\sqrt{2} \times c'$ supercell of the cubic α -FAPbI₃ and $a'2 \times b'2 \times c'$ supercell of rutile TiO₂, the lattice misfit between cubic α -FAPbI₃ and rutile TiO₂ is only \approx 1.9%, and this makes the heterostructures composed by these two materials ideal for the theoretical study. The absorption spectra computed using the TD-DFT method are shown in Figure S2 (Supporting Information). The cubic structure gives a blueshifted main peak, compared with the trigonal one. Two possible interfacial structures, i.e., PbI₂/TiO₂ and FAI/TiO₂ interfaces, are taken into account for making the interface contact layers. The optimized structures for PbI2/TiO2 and FAI/TiO₂ interfaces are shown in Figure 1, and the optimized lattice parameters are listed in Table 1. For PbI₂/TiO₂ interface, the lattice constant is ≈ 0.1 Å smaller than the organic layer-mediated interface, indicating that the interfacial bonds are much stronger in the inorganic/TiO₂ interface. The bond lengths in the different interfaces are listed in Table 2. The interfaces with labeled atoms are shown in Figure S3 (Supporting Information). The interfacial in PbI₂/TiO₂-mediated heterojunction is mainly attributed to the Pb-O and Pb-I bonds, and the inorganic bonding in the PbI₂/TiO₂ interface is stronger than the organic counterpart, i.e., hydrogen bonding, in FAI/TiO₂ interface. As a result, the Pb-I bonds are $\approx 0.3-0.5$ Å longer than those in the α -FAPbI₃, and this behavior is closely related to the enhanced Pb-O bonding across the interface. On the other hand, the H-O hydrogen bonds are much shorter than the Ti-I bonds, showing that the chemical bonding in FAI/TiO2 interface is mainly the hydrogen bonding. The computed optical absorption spectra for both interfacial systems are shown in Figure S4 (Supporting Information).



Figure 1. Fully relaxed interfacial structures for a) PbI_2/TiO_2 and b) FAI/ TiO₂ interfaces, respectively. Dark gray, purple, blue, red, brown, pink, and gray balls indicate the Pb, I, Ti, O, C, H, and N atoms, respectively.

Table 2. Interfacial bond lengths of Pbl_2/TiO_2 and FAI/TiO_2 after geometry optimization (in Å). Interfacial atoms in FAI/TiO_2 interface, i.e., Ti1, Ti2, I1, O1, O2, O3, O4, H1, H2, H3, and H4 and those in the Pbl_2/TiO_2 interface, i.e., Pb, Pb1, Pb2, O1, O2, O3, I1, I2, I3, and I4 are shown in Figure S3 (Supporting Information).

Bond length [Å]	FAI/TiO ₂	Pbl ₂ /TiO ₂
Ti1-I1	3.757	-
Ti2-I1	4.563	-
01-H1	2.588	_
O1-H2	1.697	-
O2-H3	1.718	-
O3-H4	2.582	-
РЬ-О1	_	2.220
Pb-O2	_	2.342
Pb-O3	_	2.313
РЬ1-11	_	3.739
РЬ1-12	_	3.591
Pb2-13	-	3.746
Pb2-14	_	3.593

3.2. External Bias Poling Exerted on the Devices

We applied two external electric fields with opposite directions to simulate the positive and negative poling on the planar perovskite devices. To this end, the saw-tooth-like dipole-corrected potential^[42,43] is implemented as

$$V_{\rm dip}(\mathbf{r}) = 4\pi m (\mathbf{r}/r_m - 1/2), \ 0 < \mathbf{r} < r_m \tag{3}$$

where *m* is the surface dipole density of the slab and r_m is the periodic length along the direction perpendicular to the slab. The total potential is given by

$$V_{\text{tot}}(\mathbf{r}) = V_{\text{per}}(\mathbf{r}) + V_{\text{ext}}(\mathbf{r}) + V_{\text{dip}}(\mathbf{r})$$
(4)

where $V_{per}(\mathbf{r})$ and $V_{ext}(\mathbf{r})$ are the periodic and external potentials, respectively. The corrected energy is written as

$$\Delta E = \int_{\Omega} \rho^{e}(\mathbf{r}) V_{dip}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int_{\Omega} \rho^{i}(\mathbf{r}) V_{dip}(\mathbf{r}) d\mathbf{r}$$

$$-\frac{1}{2} \int_{\Omega} \rho^{e}(\mathbf{r}) V_{dip}(\mathbf{r}) d\mathbf{r}$$

$$= \frac{1}{2} \int_{\Omega} \left(\rho^{i}(\mathbf{r}) + \rho^{e}(\mathbf{r}) \right) V_{dip}(\mathbf{r}) d\mathbf{r}$$
(5)

where $\rho^i(\mathbf{r})$ and $\rho^e(\mathbf{r})$ are the ionic and electronic charge density, respectively. The corrected force is given by

$$\Delta \mathbf{F} = -\frac{1}{2} \int_{\Omega} \nabla \rho^{i}(\mathbf{r}) V_{dip}(\mathbf{r}) d\mathbf{r} - \frac{1}{2} \int_{\Omega} (\rho^{i}(\mathbf{r}) + \rho^{e}(\mathbf{r})) \nabla V_{dip}(\mathbf{r}) d\mathbf{r}$$
$$= -\frac{1}{2} e Z_{I} \nabla V_{dip} - \frac{1}{2} \int_{\Omega} (\rho^{i}(\mathbf{r}) + \rho^{e}(\mathbf{r})) \nabla V_{dip}(\mathbf{r}) d\mathbf{r} \qquad (6)$$
$$= -\frac{4\pi m e Z_{I}}{r_{m}} \vec{r}_{0}$$

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Figure 2. The interfacial structures for FAI/TiO₂ interface upon a) positive, b) negative poling, and c) without bias. Dark gray, purple, blue, red, brown, pink, and gray balls indicate the Pb, I, Ti, O, C, H, and N atoms, respectively.

where Z_I is the ionic charge of ion I and \vec{r}_0 is the unit vector of z axis. We used the electric field of 1 V μ m⁻¹ which is the same magnitude as the poling voltage applied on the perovskites solar cells in the experiment.^[9] The positive and negative poling is applied on FAPbI₃/TiO₂ heterostructures by using the corresponding saw-tooth-like potentials shown in Figure S5 (Supporting Information). The dipole-corrected force was included during the ionic relaxation to mimic the real poling effect on the heterostructures, and the ionic optimization without dipole-correction was also performed to compare with the dipole-corrected case. The fully relaxed interfacial structures of FAI/TiO₂ upon positive and negative poling are shown in Figure 2. Displacement of Pb and I is clearly seen upon the positive or negative poling process while the organic moieties, i.e., HC(NH₂)₂, rotate under different poling directions. Compared with ionic drift upon external bias, the ionic displacement is hardly observed in the TiO₂ side, indicating the possibility of ionic drift in perovskites reported recently.^[9,29,30] We note that the ionic drift from perovskites is observed not only along the poling direction but also in the plane perpendicular to the field, owing to the interfacial interactions. The band alignment of the heterostructure is shown in Figure S6 (Supporting Information). The photogenerated electrons can flow from the perovskites part to the TiO₂ part under positive poling. The PbI₂/TiO₂ interface under electric field is discussed in Section 3.4.

3.3. Charge Transport in the Organic Interface-Mediated Heterostructure

The charge difference between the FAPbI₃/TiO₂ heterostructures and two separated fragments can be used to describe the charge transport in the heterojunctions. The depletion and accumulation of charge across the FAI/TiO₂ interface is shown in Figure 3. The corresponding charge transfer upon positive and negative poling is shown in Figures 4 and 5, respectively. The charge transport mainly occurs in the vicinity of the interface due to both the hydrogen bond and Ti-O bond in the interfacial region. It can be seen that the depleted charge mainly takes place at O 2p and I 5p orbitals and transfers to the O 2s and I 5s orbitals. When the electric field is aligned from electron transporting layer (ETL) to perovskite side, i.e., positive poling, we find that Ti 4s and Pb 6s orbitals and the organic moieties are also involved in the charge transfer process due to the ion displacement. As shown in Figure 4, by applying a positive external field, the electrons are transferred to the TiO_2 near the front contacting layer, and the carrier tunneling through the high-resistance TiO₂ can lead to the transfer of electrons to the anode. Thus, an enhanced PCE, *I–V* character, and switchable photovoltaic performance are resulted upon positive poling. The switchable photovoltaic effect in hybrid perovskites is associated with the long range electromigration.^[44] It is worth mentioning that large



Figure 3. The a) depletion of charge density and b) accumulated charge across the interfacial region for FAI/TiO₂ interface.



Figure 4. The a) depletion of charge density and b) accumulated charge across the interfacial region upon positive poling for FAI/TiO2 interface.

amount of charge accumulation takes place at the organic part $HC(NH_2)_2$ due to the rotation of the organic moieties, together with the ion displacement and orbital reorientation. On the other hand, the negative poling leads to the carrier transfer toward the perovskites side close to the hole transport materials, and further the recombination of the electrons and holes. Thus, weaker photoinduced current and device performance occurs upon negative poling. The charge depletion or accumulation upon external positive or negative electric field without dipole-correction is shown in Figures S7 and S8 (Supporting Information), respectively.

The charge difference integrated over the *xy* plane and the charge displacement curve (CDC) are informative for analyzing the charge transfer in the heterostructure. The charge difference integrated over the *xy* plane is given by

$$\Delta q = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left(\rho_{FAPbI_3/TiO_2} - \rho_{FAPbI_3} - \rho_{TiO_2} \right) dx \, dy \tag{7}$$

The CDC is calculated by integrating $\triangle q$ along *z* as

$$\Delta Q = \int_{-\infty}^{z} \Delta q \, \mathrm{d}z \tag{8}$$

The $\triangle q$ and $\triangle Q$ for FAI/TiO₂ interface prior to and after positive and negative poling are shown in Figures 6-8, respectively. The electrons transport from the perovskite side to the ETL, and are confined within the interfacial region, indicating that the photoinduced charge is trapped near the interface. Upon positive bias poling, large amount of fieldinduced charge can move along the built-in photogenerated field shown in Figure 9. When field-induced electrons are near the vicinity of the interface, some are trapped in the interface while most of them move to the front contacting layer and the anode, resulting in enhanced photovoltaic performance. Under the negative poling, most field-induced electrons are moved to the perovskite side and then to the back electrode. The relatively flat CDC curve in TiO₂ side (Figure 8) reflects that the electron transfer no longer occurs in the vicinity of the front contacting region. The $\triangle q$ and $\triangle Q$ at the FAI/TiO2 interface under the positive field without dipole-correction (Figure S9, Supporting Information) do not show much difference from the case without the external field. The positive poling field results in much more electron accumulation at the interfacial region, compared to the negative poling field. This is because the positive field is along



Figure 5. The a) depletion of charge density and b) accumulated charge across the interfacial region upon negative poling for FAI/TiO₂ interface.



Figure 6. The planar integral in the xy plane of a) charge density difference and b) the integrated charge transfer along the z-direction across the interfacial region for FAI/TiO2 interface.

the photogenerated built-in field (Figure 9), leading to much more electrons across the FAPbI₃/TiO₂ heterostructure. The charge transfer in PbI₂/TiO₂ interface is discussed below.

3.4. Electronic Characteristics upon Switchable Bias

The total density of states (TDOS) of the FAI/TiO2 interface prior to and after applying the electric field is shown in Figure 10. Without the electric field, the FAI/TiO₂ interface gives a band gap of 1.47 eV, in good agreement with the band gap of pure FAPbI₃.^[10] Upon negative bias the band gap increases slightly to 1.55 eV due to the ionic drift, orbital and charge reorientation, while the valence band maximum (VBM) and conduction band minimum (CBM) do not change much compared to the case without the external field. The electronic conduction occurs upon the positive bias. The CBM and VBM



Figure 7. The planar integral in the xy plane of a) charge density difference and b) the integrated charge transfer along the z-direction across the interfacial region upon positive poling for FAI/TiO2 interface.

www.MaterialsViews.com 8 (a) 4 0 FAPbI, -4 TiO -8 10 (b) 5 FAPbI. TiO, 0 Electric field (Negative poling) -5 -10 Interface 25 20 10 5 15 0 Distance(Å) Figure 8. The planar integral in the xy plane of a) charge density differ-

Aq(electron)

ΔQ(electron)

ence and b) the integrated charge transfer along the z-direction across the interfacial region upon negative poling for FAI/TiO₂ interface.

change significantly by the positive voltage poling while the states corresponding to CBM and VBM at the negative bias are similar to those without external field. This switchable diode effect, controlled by the electric field, is associated with the ion diffusion, ferroelectric reordering, and charge redistribution under the external field.

The partial density of states (PDOS) due to Ti 4s and 3d, O 2s, and I 5s and 5p orbitals prior to and after positive bias is shown in Figure 11. For the heterostructure at zero bias, the states corresponding to VBM stem from the I 5p orbitals while those corresponding to CBM stem from the I 5p, O 2s, Ti 3d, Ti 4s, and I 5s orbitals, indicating possible optical transitions among these orbitals. Apparently, except I 5p states, the Ti 3d, I 5s, and O 2s states are involved in the electronic conduction upon positive bias poling. Compared with the PDOS without poling, the Ti 3d states in the conduction band are pushed toward the Fermi level, leading to much enhanced electric



Figure 9. The microscopic (black line) and macroscopic (red line) planeaveraged potential across the interfacial region for FAI/TiO₂ interface.



Figure 10. Computed TDOS of the FAI/TiO_2 mediated heterostructure a) prior to and b) after positive and c) negative poling. Zero is set to the top of the valence band.

current through the FAI/TiO₂ interface to the front contact layer. The role of the Ti 3d states in the electronic conduction is consistent with the charge transport (Figure 4) and the CDC analysis (Figure 7).^[27] Hence, a switchable photovoltaic property controlled by the external voltage is expected to arise in the FAI/TiO₂ interface-mediated planar perovskite solar devices, as shown in the experiments.^[9] This electric field driven diode effect may find applications in future optoelectronic devices, memristors, and circuits.

In contrast, the switchable diode effect is not seen in the PbI₂/TiO₂-mediated interface. The TDOS and PDOS of the PbI₂/TiO₂-mediated interface upon positive poling and without poling are shown in **Figure 12**. The band gap is reduced from 0.40 to 0.20 eV with the positive poling while the VBM and CBM remain unchanged, indicating that the structure and the electronic characteristics do not show much difference with or without the external electric field. This is because the applied field (1 V μ m⁻¹) is much weaker than the built-in field across the



Figure 11. Computed PDOS of the FAI/TiO $_2$ mediated heterostructure a) prior to and b) after positive poling. Zero is set to the top of the valence band.



Figure 12. Computed TDOS of the Pbl_2/TiO_2 mediated heterostructure a) prior to and b) after positive poling. c) PDOS of the heterostructure upon positive bias is also given. Zero is set to the top of the valence band.



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PbI2/TiO2 interface. The plane-averaged electrostatic potential across the interface is shown in Figure S10 (Supporting Information). As a result, little movement of interfacial ions occurs when the external electric field is applied, and the accumulated charge is also confined in the interface without moving across the TiO₂ side. The depletion and accumulation of charge at the PbI2/TiO2 interface prior to and after the positive poling are shown in Figures S11 and S12 (Supporting Information), respectively, while for the case without the dipole-correction, the depletion and accumulation of charge and the corresponding $\triangle q$ and $\triangle Q$ are shown in Figures S13–S15 (Supporting Information), respectively. Moreover, the stabilized interfacial structure is related to the heavy Pb atoms which have a relatively higher activation energy of 0.80 eV compared with organic moieties and the halide atoms.^[30] The stereochemical activity of the lone pair of Pb 6s and I 5s in the interface plays some roles in the screening of the external voltage, and it leads to the weak electric-field effect. The lone pairs of Pb and I are confirmed by the higher number of states of Pb 6p and I 5p in the vicinity of the VBM and CBM (Figure 12). The weaker response of the PbI₂/TiO₂ interface under the electric field is further confirmed by the spontaneous polarization of the corresponding perovskites part in the heterostructures. A spontaneous polarization of 18.69 μ C cm⁻² is found for perovskite part in the FAI/TiO₂ interface while a smaller value of 0.89 μ C cm⁻² for the PbI₂/ TiO₂ interface is calculated based on the modern theory of polarization.^[40,41] The strong ferroelectricity of the organicmediated interface reflects the rotation and ferroelectric redistribution of the organic moieties under the external field. This also explains why the FAI/TiO₂ interface exhibits a switchable photovoltaic diode effect while the inorganic-mediated interface does not upon positive bias. Spin-orbit coupling (SOC) always underestimates the band gap of the hybrid perovskites.^[45] In order to check the validity of the pure DFT calculations, we performed the DFT+SOC calculations for the FAI/TiO₂ interface prior to and after negative poling, and the corresponding TDOS are shown in Figure S16 (Supporting Information). It is clear that the electronic properties including the band characters

4. Conclusion

DFT computation based analysis of the charge difference between the α -HC(NH₂)₂PbI₃/TiO₂ complex and the two separated components shows that the photoinduced charges are confined in the vicinity of the FAI/TiO2 and PbI2/TiO2 mediated interfacial regions. The positive poling field is along the same direction as the built-in electrostatic filed across the heterostructures, and drives charge accumulation in the FAI/ TiO₂ interface. The accumulated charges flow through the high-resistance TiO₂ ETL toward the front contacting window layer, leading to notable electronic conduction across the planar perovskite cell with enhanced device performance. The TDOS and PDOS for the heterojunction prior to and after applying the external voltage show that the band gap of 1.47 eV is slightly increased to 1.55 eV for the heterostructure under the negative poling, whereas the VBM and CBM remain almost unchanged upon the negative bias poling. The band gap is reduced to zero

remain unchanged compared with the DFT calculations.

upon applying the positive field, while the electronic conduction is closely related to the reorientation of the ferroelectric polarization and the ionic mobility in the inorganic–organic hybrid halide perovskites. The PbI_2/TiO_2 -mediated interface does not show notable switching photovoltaic effect due to stabilization of the Pb atoms at the interface. Our study confirms the existence of the organic cation diffusion in perovskites and the charge redistribution across the interfaces. The electric-fieldcontrolled diode effect renders this new organic-layer-mediated planar heterostructure a promising candidate for highly efficient solar cells and optoelectronic devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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