Photovoltaic Diode Effect Induced by Positive Bias Poling of Organic Layer-Mediated Interface in Perovskite Heterostructure \( \alpha\text{-HC(NH}_2\text{)}_2\text{PbI}_3/\text{TiO}_2 \)

Hong-Jian Feng,* Jinsong Huang, and Xiao Cheng Zeng*

It is shown that in the formamidinium (FA) lead iodide/titania heterostructure \( \alpha\text{-HC(NH}_2\text{)}_2\text{PbI}_3/\text{TiO}_2 \), the organic layer-mediated interface, i.e., FAI/TiO\(_2\), 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/TiO\(_2\) gives rise to a strong polarization of 18.69 \( \mu \)C cm\(^{-2}\), compared to that (0.89 \( \mu \)C cm\(^{-2}\)) in the inorganic layer-mediated interface PbI\(_2\)/TiO\(_2\). 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/TiO\(_2\) upon the positive bias poling. The latter effect also provides an explanation on why the FAPbI\(_3\)-based devices can largely reduce the scanning hysteresis in the \( J-V \) curves (Yang et al., \textit{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 in electrically and optically readable memristors and circuits.\(^{[9]}\) Methylammonium lead iodide CH\(_3\)NH\(_3\)PbI\(_3\) (MAPbI\(_3\)) is the prototype inorganic–organic 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(NH\(_2\))\(_2\), giving another organic molecule HC(NH\(_2\))\(_2\)/(FA) that exhibits the trigonal structure with the \( P\text{3}m\text{1} \) space group which can be changed to the yellow hexagonal nonperovskite phase (\( \delta \) phase) with space group \( P\text{6}_3\text{mc} \) at an ambient atmosphere.\(^{[4]}\) The \( \delta \) phase possesses a corner-sharing PbI\(_6\) octahedral network while the hexagonal phase exhibits a face-sharing PbI\(_6\) 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 FAPbI\(_3\) at 298 K, and, interestingly, the cubic structure with \( \text{Im}3\text{m} \) space group was obtained.\(^{[10]}\) The black FAPbI\(_3\) 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 \( \alpha\)FAPbI\(_3\).

To date, the carrier separation and charge transfer at the interface of planar hybrid perovskites/TiO\(_2\) 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/TiO\(_2\) heterostructure have been published in the literature due in part to the relatively large lattice mismatch between MAPbI\(_3\) and anatase TiO\(_2\). To address this issue in DFT computation, a larger supercell is needed to reduce or remove the in-plane strain...
involved when constructing the heterostructure.\textsuperscript{[25,26]} Thus far, the MAPbI\textsubscript{3}\textsubscript{Cl\textsubscript{x}}/TiO\textsubscript{2} interface with a large supercell has been optimized based on the numerical pseudopotasis basis (the plane-wave basis would be computationally very demanding).\textsuperscript{[25,26]} However, the charge transfer mechanism is still incompletely understood. Previously, we have systematically investigated the charge accumulation at the interface of CH\textsubscript{3}NH\textsubscript{3}Sn\textsubscript{i}Pb\textsubscript{j}Pb\textsubscript{k}/TiO\textsubscript{2} heterostructures with \pm6\% in-plane strain by using DFT and time-dependent DFT (TD-DFT).\textsuperscript{[27]} We suggest that the charge transfer is related to the built-in field across the interface.\textsuperscript{[27]}

In this study, the lattice misfit between the cubic FAPbI\textsubscript{3} and rutile TiO\textsubscript{2}\textsuperscript{[28]} is merely \pm1.9\% when using the \(a'\sqrt{2} \times b'\sqrt{2} \times c'\) supercell of the cubic FAPbI\textsubscript{3} and the \(a'2 \times b'2 \times c'\) supercell of rutile TiO\textsubscript{2} to build the heterostructure. As such, the charge transport in the \(\alpha\)-HC(NH\textsubscript{3})\textsubscript{3}PbI\textsubscript{3}/TiO\textsubscript{2} 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.\textsuperscript{[3]} Remarkably, the forward and reverse scanning hysteresis of the \(J–V\) curves can be largely reduced when the FAPbI\textsubscript{3}-based devices are adopted.\textsuperscript{[8]} This interesting behavior is apparently associated with the ionic diffusion and defect mobility upon bias poling on the solar devices.\textsuperscript{[9,29,30]} The hysteresis in \(J–V\) 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 PbI\textsubscript{6} 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 \(J–V\) hysteresis,\textsuperscript{[31]} and that the interfacial structure itself also plays certain role in the \(J–V\) hysteresis.\textsuperscript{[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 \(\alpha\)-FAPbI\textsubscript{3}/TiO\textsubscript{2} 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 FAPbI\textsubscript{3}/TiO\textsubscript{2}-based solar devices that give the highest efficiency.\textsuperscript{[38]}

2. Computational Methods

We used Quantum ESPRESSO package to perform the DFT and TD-DFT computations.\textsuperscript{[33–35]} The exchange correlation interactions are described by the Perdew–Burke–Ernzerhof (PBE) parameterization of the generalized gradient approximation for solid (PBEsol).\textsuperscript{[36]} The interactions between valence electrons and ions are described by the GBRV ultrasoft pseudopotential.\textsuperscript{[37]} \(a'\sqrt{2} \times b'\sqrt{2} \times c'\) supercell of the cubic FAPbI\textsubscript{3} and \(a'2 \times b'2 \times c'\) supercell of rutile TiO\textsubscript{2} are used to build the interfacial heterostructures. The lattice parameters for bulk FAPbI\textsubscript{3} and TiO\textsubscript{2} are taken from the experimental measurements. We considered two possible interfaces for \(\alpha\)-HC(NH\textsubscript{3})\textsubscript{3}PbI\textsubscript{3}/TiO\textsubscript{2} heterostructure, i.e., PbI\textsubscript{2}/TiO\textsubscript{2} and FAI/TiO\textsubscript{2} 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 PbI\textsubscript{2}/TiO\textsubscript{2}, FAI/TiO\textsubscript{2} interfaces, bulk FAPbI\textsubscript{3}, and TiO\textsubscript{2} are given in Table 1.

<table>
<thead>
<tr>
<th>Structure</th>
<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
<th>(\alpha = \beta = \gamma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbI\textsubscript{2}/TiO\textsubscript{2} (Opt.)</td>
<td>9.188</td>
<td>9.188</td>
<td>25.856</td>
<td>90</td>
</tr>
<tr>
<td>FAI/TiO\textsubscript{2} (Opt.)</td>
<td>9.288</td>
<td>9.288</td>
<td>25.856</td>
<td>90</td>
</tr>
<tr>
<td>(\alpha)-FAPbI\textsubscript{3} (Exp.)\textsuperscript{[11]}</td>
<td>8.997</td>
<td>8.997</td>
<td>6.362</td>
<td>90</td>
</tr>
<tr>
<td>Rutile-TiO\textsubscript{2} (Exp.)\textsuperscript{[28]}</td>
<td>9.174</td>
<td>9.174</td>
<td>2.954</td>
<td>90</td>
</tr>
<tr>
<td>(\alpha)-FAPbI\textsubscript{3} (Exp.)\textsuperscript{[11]}</td>
<td>6.362</td>
<td>6.362</td>
<td>6.362</td>
<td>90</td>
</tr>
<tr>
<td>Rutile-TiO\textsubscript{2} (Exp.)\textsuperscript{[28]}</td>
<td>4.587</td>
<td>4.587</td>
<td>2.954</td>
<td>90</td>
</tr>
</tbody>
</table>

\(\alpha\)-HC(NH\textsubscript{3})\textsubscript{3}PbI\textsubscript{3} (Exp.)\textsuperscript{[11]} is merely 8.997 8.997 6.362 90 when using the \(a'\sqrt{2} \times b'\sqrt{2} \times c'\) supercell of the cubic FAPbI\textsubscript{3} and \(a'2 \times b'2 \times c'\) supercell of rutile TiO\textsubscript{2} are used to build the heterostructures. The lattice constants for \(\alpha\)-FAPbI\textsubscript{3} and rutile TiO\textsubscript{2} is only \pm 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.

Table 1. Fully relaxed lattice constants for PbI\textsubscript{2}/TiO\textsubscript{2} (a), FAI/TiO\textsubscript{2} (b) interfaces, cubic formamidinium lead iodide, and rutile TiO\textsubscript{2}, \(a'\sqrt{2} \times b'\sqrt{2} \times c'\) supercell of the \(\alpha\)-FAPbI\textsubscript{3} and \(a'2 \times b'2 \times c'\) supercell of rutile TiO\textsubscript{2} are used to construct the heterostructures. The lattice misfit between \(\alpha\)-FAPbI\textsubscript{3} and rutile TiO\textsubscript{2} is only \pm 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.

3. Results and Discussion

3.1. Cubic and Trigonal \(\alpha\)-FAPbI\textsubscript{3} and Interfacial Structures of FAPbI\textsubscript{3}/TiO\textsubscript{2} Heterostructures

The crystal structures of the cubic and trigonal \(\alpha\)-FAPbI\textsubscript{3} are shown in Figure S1 (Supporting Information). The cubic...
phase with \( \text{pm}3\text{m} \) 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 \( \alpha-\text{FAPbI}_3 \) and \( a' \times b' \times c' \) supercell of rutile \( \text{TiO}_2 \), the lattice mismatch between cubic \( \alpha-\text{FAPbI}_3 \) and rutile \( \text{TiO}_2 \) 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., \( \text{PbI}_2/\text{TiO}_2 \) and \( \text{FAI}/\text{TiO}_2 \) interfaces, are taken into account for making the interface contact layers. The optimized structures for \( \text{PbI}_2/\text{TiO}_2 \) and \( \text{FAI}/\text{TiO}_2 \) interfaces are shown in Figure 1, and the optimized lattice parameters are listed in Table 1. For \( \text{PbI}_2/\text{TiO}_2 \) interface, the lattice constant is \( \approx 0.1 \) Å smaller than the organic layer-mediated interface, indicating that the interfacial bonds are much stronger in the inorganic/\( \text{TiO}_2 \) 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 \( \text{PbI}_2/\text{TiO}_2 \)-mediated heterojunction is mainly attributed to the \( \text{Pb}–\text{O} \) and \( \text{Pb}–\text{I} \) bonds, and the inorganic bonding in the \( \text{PbI}_2/\text{TiO}_2 \) interface is stronger than the organic counterpart, i.e., hydrogen bonding. The computed optical absorption spectra for both interfacial systems are shown in Figure S4 (Supporting Information).

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

\[
V_{\text{dip}}(\mathbf{r}) = 4\pi m(\mathbf{r}/r_m - 1/2), \quad 0 < r < r_m
\]

(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

\[
V_{\text{tot}}(\mathbf{r}) = V_{\text{pol}}(\mathbf{r}) + V_{\text{ext}}(\mathbf{r}) + V_{\text{dip}}(\mathbf{r})
\]

(4)

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

\[
\Delta E = \int_{\Omega} \rho^+ (\mathbf{r}) V_{\text{dip}}(\mathbf{r}) \, d\mathbf{r} - \frac{1}{2} \int_{\Omega} \rho^+ (\mathbf{r}) V_{\text{dip}}(\mathbf{r}) \, d\mathbf{r} - \frac{1}{2} \int_{\Omega} (\rho^+ (\mathbf{r}) + \rho^- (\mathbf{r})) V_{\text{dip}}(\mathbf{r}) \, d\mathbf{r}
\]

(5)

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

\[
\Delta F = -\frac{1}{2} \int_{\Omega} \nabla \rho^- (\mathbf{r}) V_{\text{dip}}(\mathbf{r}) \, d\mathbf{r} - \frac{1}{2} \int_{\Omega} (\rho^+ (\mathbf{r}) + \rho^- (\mathbf{r})) \nabla V_{\text{dip}}(\mathbf{r}) \, d\mathbf{r}
\]

(6)

\[
= -\frac{1}{2} c Z_i \nabla V_{\text{dip}} - \frac{1}{2} \int_{\Omega} (\rho^+ (\mathbf{r}) + \rho^- (\mathbf{r})) \nabla V_{\text{dip}}(\mathbf{r}) \, d\mathbf{r}
\]

\[
= -\frac{4\pi mcZ_i}{r_m} \frac{V_{\text{dip}}(\mathbf{r})}{r_0}
\]

### Table 2. Interfacial bond lengths of \( \text{PbI}_2/\text{TiO}_2 \) and \( \text{FAI}/\text{TiO}_2 \) after geometry optimization (in Å).

<table>
<thead>
<tr>
<th>Bond length [Å]</th>
<th>( \text{FAI}/\text{TiO}_2 )</th>
<th>( \text{PbI}_2/\text{TiO}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ti}-\text{I} )</td>
<td>3.757</td>
<td>–</td>
</tr>
<tr>
<td>( \text{Ti}_2-\text{I} )</td>
<td>4.563</td>
<td>–</td>
</tr>
<tr>
<td>( \text{O}_1-\text{H} )</td>
<td>2.588</td>
<td>–</td>
</tr>
<tr>
<td>( \text{O}_1-\text{H}_2 )</td>
<td>1.697</td>
<td>–</td>
</tr>
<tr>
<td>( \text{O}_2-\text{H}_3 )</td>
<td>1.718</td>
<td>–</td>
</tr>
<tr>
<td>( \text{O}_3-\text{H}_4 )</td>
<td>2.582</td>
<td>–</td>
</tr>
<tr>
<td>( \text{Pb}_0-\text{O} )</td>
<td>2.220</td>
<td>3.491</td>
</tr>
<tr>
<td>( \text{Pb}_0-\text{O}_2 )</td>
<td>2.342</td>
<td>3.491</td>
</tr>
<tr>
<td>( \text{Pb}_0-\text{O}_3 )</td>
<td>2.313</td>
<td>3.491</td>
</tr>
<tr>
<td>( \text{Pb}_1-\text{I} )</td>
<td>3.739</td>
<td>3.491</td>
</tr>
<tr>
<td>( \text{Pb}_1-\text{I}_2 )</td>
<td>3.591</td>
<td>3.491</td>
</tr>
<tr>
<td>( \text{Pb}_2-\text{I} )</td>
<td>3.746</td>
<td>3.491</td>
</tr>
<tr>
<td>( \text{Pb}_2-\text{I}_2 )</td>
<td>3.593</td>
<td>3.491</td>
</tr>
</tbody>
</table>

Figure 1. Fully relaxed interfacial structures for a) \( \text{PbI}_2/\text{TiO}_2 \) and b) \( \text{FAI}/\text{TiO}_2 \) interfaces, respectively. Dark gray, purple, blue, red, brown, pink, and gray balls indicate the \( \text{Pb}, \text{I}, \text{Ti}, \text{O}, \text{C}, \text{H}, \) and \( \text{N} \) atoms, respectively.
where \( Z_i \) is the ionic charge of ion \( i \) and \( \vec{n} \) is the unit vector of \( z \) axis. We used the electric field of 1 V \( \mu \text{m}^{-1} \) which is the same magnitude as the poling voltage applied on the perovskite solar cells in the experiment.\(^{9}\) The positive and negative poling is applied on FAPbI\(_3\)/TiO\(_2\) 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/TiO\(_2\) 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(NH\(_2\))\(_2\), rotate under different poling directions. Compared with ionic drift upon external bias, the ionic displacement is hardly observed in the TiO\(_2\) 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 perovskite part to the TiO\(_2\) part under positive poling. The PbI\(_2\)/TiO\(_2\) 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 FAPbI\(_3\)/TiO\(_2\) 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/TiO\(_2\) 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 TiO\(_2\) can lead to the transfer of electrons to the anode. Thus, an enhanced PCE, \( J–V \) 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

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**Figure 2.** The interfacial structures for FAI/TiO\(_2\) 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.

**Figure 3.** The a) depletion of charge density and b) accumulated charge across the interfacial region for FAI/TiO\(_2\) interface.
amount of charge accumulation takes place at the organic part \( \text{HC(NH}_2\text{)}_2 \) 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

\[
\Delta q = \int \int (\rho_{\text{FAI/TiO}_2} - \rho_{\text{FAI}} - \rho_{\text{TiO}_2}) \, dx \, dy
\]  

(7)

The CDC is calculated by integrating \( \Delta q \) along \( z \) as

\[
\Delta Q = \int \Delta q \, dz
\]  

(8)

The \( \Delta q \) and \( \Delta Q \) for FAI/TiO\(_2\) 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 field-induced 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 TiO\(_2\) side (Figure 8) reflects that the electron transfer no longer occurs in the vicinity of the front contacting region. The \( \Delta q \) and \( \Delta Q \) at the FAI/TiO\(_2\) 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
the photogenerated built-in field (Figure 9), leading to much more electrons across the FAPbI$_3$/TiO$_2$ heterostructure. The charge transfer in PbI$_2$/TiO$_2$ interface is discussed below.

### 3.4. Electronic Characteristics upon Switchable Bias

The total density of states (TDOS) of the FAI/TiO$_2$ interface prior to and after applying the electric field is shown in Figure 10. Without the electric field, the FAI/TiO$_2$ interface gives a band gap of 1.47 eV, in good agreement with the band gap of pure FAPbI$_3$.[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 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

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**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/TiO$_2$ interface.

**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/TiO$_2$ interface.

**Figure 8.** 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 negative poling for FAI/TiO$_2$ interface.

**Figure 9.** The microscopic (black line) and macroscopic (red line) plane-averaged potential across the interfacial region for FAI/TiO$_2$ interface.

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current through the FAI/TiO\textsubscript{2} 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).\cite{27} Hence, a switchable photovoltaic property controlled by the external voltage is expected to arise in the FAI/TiO\textsubscript{2} interface-mediated planar perovskite solar devices, as shown in the experiments.\cite{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 PbI\textsubscript{2}/TiO\textsubscript{2}-mediated interface. The TDOS and PDOS of the PbI\textsubscript{2}/TiO\textsubscript{2}-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 \textmu m\textsuperscript{-1}) is much weaker than the built-in field across the

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**Figure 10.** Computed TDOS of the FAI/TiO\textsubscript{2} mediated heterostructure a) prior to and b) after positive and c) negative poling. Zero is set to the top of the valence band.

**Figure 11.** Computed PDOS of the FAI/TiO\textsubscript{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 PbI\textsubscript{2}/TiO\textsubscript{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.
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 Δq and ΔQ 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. 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 18.60 μC cm⁻² is found for perovskite part in the FAI/TiO₂ interface while a smaller value of 0.89 μC cm⁻² for the PbI₂/TiO₂ interface is calculated based on the modern theory of polarization. The strong ferroelectricity of the organic-mediated interface is related to 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. 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 remain unchanged compared with the DFT calculations.

4. Conclusion

DFT computation based analysis of the charge difference between the α-HC(NH₂)₂PbI₂/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 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 PbI₂/TiO₂-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-field-controlled 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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