Electron transport at TiO$_2$/perovskite interfaces by considering the defect effects: a first-principles insight

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Abstract. The interface property of perovskite solar cells (PSCs) is very important, which can influence the electron transmission efficiency and stability of the cells. In this text, we have discussed the stability and bonding characteristics of PbI$_2$/TiO$_2$ interfaces by using the first-principles method. The PbI$_2$/TiO$_2$ interfaces have a high interfacial binding energy of -0.93 J/m$^2$, where the Ti-I and Pb-O bonds could form. Furthermore, the electron transport at the interfaces has been analyzed by the partial density of states by comparing the clean interfaces and interfaces with different defects. The results show that the clean PbI$_2$/TiO$_2$ interfaces could cause a stronger internal electric field, which might make the electron-hole pairs separate more easily at the interfaces. Also, it is found that common defects V$_i$ and I$_i$ are relatively easy to form at the interfaces. Some defects at low concentrations might have little effect on the electron transport at the interfaces, while they are harmful only when the concentration increases. However, V$_{Pb}$ with a high formation energy could adversely affect the electron transmission even at low concentrations. Controlling the defects at the interfaces is essential to improve the power conversion efficiencies (PCEs) and stability of PSCs.

1. Introduction

The PSCs have been recognized as a promising solar cell in recent years. The PCEs of PSCs have raised from 3.8% in the first report to 25.2% in recent work[1,2]. The PSCs are not only manufactured at a low cost, but also easy to prepare by various synthetic methods, and can be coated on a flexible substrate. Also, it has high carrier mobility, high light absorption coefficient and long electronic-hole diffusion length[3]. All these excellent features make it a most important solar cell in recent years.

The PSCs are generally a sandwich structure, with a perovskite light absorbing layer in the middle, an electron transport layer (ETL) and a hole transport layer (HTL) on both sides, and a transparent conductive glass and a metal electrode on the outermost side. When these layers are stacked together, many interfaces are inevitably produced. During the operation of the PSCs, electrons must be transferred across the interface. Therefore, the adhesion and defect characteristics at the interface have an important impact on the stability of the PSCs and the efficiency of electron transmission. Therefore, many researchers pay attention to the interface properties, and it is well recognized that interface engineering...
is essential to achieve high-performance and stable PSCs.

In PSCs, the electron transport layer is in charge of the light-excited electrons transmission from the perovskite layer to the electrode, and is an important part of the PSCs. Many materials can be used as the ETL, for example TiO$_2$, SnO$_2$, ZnO, Zn$_2$SnO$_4$. TiO$_2$ is a commonly used ETL in PSCs because of its suitable CBM and low cost. The PCE of PSCs using Li$_2$CO$_3$-doped TiO$_2$ as the electron transport layer has exceeded 25%[4].

Many researchers use various methods to increase the electron transport properties of perovskite and TiO$_2$ interfaces to increase the PCE of PSCs. Yella et al. have found that when rutile TiO$_2$ is employed as ETL, the efficiency of PSCs is higher than that of anatase TiO$_2$. They believe this is because the nanocrystalline rutile TiO$_2$ and CH$_3$NH$_3$PbI$_3$ layer form a intimate junction with large interfacial area[5]. Zhao et al. have demonstrated that imparting Al ions to the TiO$_2$/CH$_3$NH$_3$PbI$_3$ interface to generate Al$_2$TiO$_5$ can increase the average PCE of PSCs from 15.4% to 17.2%, and can also extend the electron lifetime by three times[6]. Ma et al. used NaCl doping to passivate the TiO$_2$/perovskite interface, which effectively promoted charge transport at the interface[7]. Ma et al. observed that the stability of the PSCs was significantly improved when the CdS layers had been inserted into the interface of TiO$_2$/perovskite. It was also found that the recombination between the trapped electrons and perovskite was inhibited and the efficiency of device was largely increased[8]. Guo et al. used phenyl-C$_6$1-butyric acid methylester (PC61BM) diaphragm or fullerene (C$_6$0) self-assembled monolayer (SAM) or the combination of them to modify TiO$_2$/perovskite interfaces, and found that interface modification improved the interface contact, increased the efficiency of electron extraction and collection, and raised the PCE of PSCs[9].

Many researchers have confirmed that interface properties affect the stability and PCE of PSCs, as well as the electronic transmission process. Improving the electron transmission efficiency at the interface is very important for the PCE improvement of PSCs. To address the electron transport properties, we will systematically study the atomic and electronic structures of the TiO$_2$/perovskite interface by considering the defect effects in this paper. The paper also includes the following parts. Section 2 presents the computational details and the theoretical methods. In Section 3, the interfacial properties of the clean heterointerfaces are described, and the defect effects on the electron transport at the interface are also explored. Section 4 provides a brief summary of the full text.

2. Computational Methods
We used the Vienna Ab-initio Simulation Package (VASP) for first-principles calculations in the DFT framework[10]. Simultaneously the projector augmented wave method was employed to describe the electron-ion interaction[11]. We set the energy cutoff for the plane wave basis to 500 eV in all calculations. In the simulation, an empirical pair-wise corrections proposed by Grimme in terms of DFT+D2 scheme had also been included for more precisely depicting the dispersion interactions in the systems[12]. In the structural optimization of bulk and interface systems, the pseudopotential we employed was the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) form[13]. We calculated all the electronic properties using the Heyd-Scuseria-Ernzerhof (HSE) screened hybrid functional (HSE06) to ensure the accuracy of the electron transport properties at the interface[14].
Figure 1. The optimized stable geometry of the PbI$_2$/TiO$_2$ interfaces: (a) Side view of the rutile /CH$_3$NH$_3$PbI$_3$ interface; (b) Top view of the rutile substrate (Black: Pb; Purple: I; Blue: N; Gold: C; Pink: H; Red: O; Cyan: Ti).

TiO$_2$ has two forms: rutile and anatase. At the same time, along the c axis, the end of CH$_3$NH$_3$PbI$_3$ perovskite has two types of surfaces: MAI end with $I^-$ and MA$^+$ ions, and PbI$_2$ end with $I^-$ and Pb$^{2+}$ ions. Therefore, four different interfaces can be produced. Through the previous calculations, Geng et al. had found the PbI$_2$/rutile interface has the largest binding energy\[15\]. Therefore, the research in this paper focuses on the PbI$_2$/rutile PbI$_3$ interface. We construct the super unit of the heterogeneous interface by connecting the TiO$_2$ plate and the 7 PbI$_2$ end-capped perovskite plate and vacuuming 20Å along the non-periodic direction, as shown in figure 1(a). The TiO$_2$ slab contains 10 TiO$_2$ unit, namely 60 atoms. The perovskite slab contains 6.5 MAPbI$_3$ unit with 78 atoms. The bottom layer of atoms are pinned to simulate the bulk environment. The related k-point arrangement is 4×4×1. The calculated parameters of bulk tetragonal CH$_3$NH$_3$PbI$_3$ perovskites are a=8.69 and c=12.80 Å, which match well with the previous results from the DFT calculations and experiment observations. In order to build a typical TiO$_2$/perovskite interface, we also optimized the lattice constants of rutile (a=4.66 Å, c=2.97 Å), which are in good agreement with other researches. Then, we constrained the lattice constants of the perovskite slab with these of the TiO$_2$ slab, which is always employed as the substrate in experiments.

3. Results and Discussion

3.1 The bonding characteristics and stability of rutile /CH$_3$NH$_3$PbI$_3$ interfaces

First, we calculated the interfacial adhesion energy ($E_{ad}$), which can evaluate the stability of the rutile /CH$_3$NH$_3$PbI$_3$ interface, which is defined as

$$E_{ad} = \frac{(E_{\text{interface}} - E_{\text{TiO}_2} - E_{\text{perovskite}})}{S}$$

(1)

Where $E_{\text{interface}}$, $E_{\text{TiO}_2}$ and $E_{\text{perovskite}}$ represent the total energies of the heterointerface supercell, the rutile substrate and the CH$_3$NH$_3$PbI$_3$ slab, respectively. S refers the area of the rutile/CH$_3$NH$_3$PbI$_3$ interface.

Table 1. The calculated interfacial adhesion energy, lattice mismatch and Bader charge of the PbI/TiO$_2$ interface.

| Interface     | Interfacial adhesion energy (J/m$^2$) | Lattice mismatch | Bader charge |
|---------------|---------------------------------------|------------------|--------------|
| PbI/TiO$_2$   | -0.93                                 | 7.25%            | -0.28        |
By using equation (1), we have obtained that the PbI$_2$/TiO$_2$ interfaces have an interfacial adhesion energy of about -0.93 J/m$^2$ as shown in Table 1. Since perovskite is generally grown on the TiO$_2$ in the experiments, its crystal cell is stretched horizontally and compressed vertically to fit the lattice constant of TiO$_2$. Next, we calculate the lattice mismatch of the TiO$_2$/perovskite heterointerfaces to be about 7.25%. When referred to the heterointerfaces of conventional CZTS/CdS solar cells (-3.05 J/m$^2$), it can be deduced that the binding at the rutile/CH$_3$NH$_3$PbI$_3$ interfaces is still comparatively weak. The calculated Bader charge of perovskite fragment is $-0.28$ e, where the negative value denotes that electron transfer from CH$_3$NH$_3$PbI$_3$ to rutile.

Table 2. The ratio of bonded anion atoms and bond length of the bonds at the interface.

| Interface    | Bond (Pb-O) | Bond (Ti-I) |
|--------------|-------------|-------------|
| PbI$_2$/SnO$_2$ | 50% 2.30    | 100% 2.87–2.93 |

Table 2 gives the detailed bonding situation of rutile/CH$_3$NH$_3$PbI$_3$ interfaces. The proportions of the bonded O atoms are 50% (Pb-O) and the bonded I atoms are 100% (Ti-I) (we define the bond number of one kind of bond as the bonded anion atoms/surface anion number), and the bond length of Pb-O is 2.30 Å and Ti-I is 2.87–2.93 Å, respectively. From the results of structural optimization, we can see the perovskite structure is maintained in the PbI$_2$/perovskite interface, and the octahedron PbI$_6$ is not distorted.

Figure 2. Electron transfer at the interface: (a) main view of the 3D charge density differences; (b) planar-averaged charge density differences along the c direction of the PbI/TiO$_2$ interfaces. The yellow area represents the electron increase, and the green area represents the electron decrease.

Furthermore, the charge density differences at the interfaces are given to clarify the interactions of different atoms. Figure 2 depicts the charge density differences (Figure 2 (a)) and planar-averaged charge density differences (Figure 2 (b)) at the PbI/TiO$_2$ interfaces. We can clearly observe the strong Pb-O and Ti-I coupling at the PbI/TiO$_2$ interfaces. Electrons are favorable to accumulate around O and I atoms (yellow region) and deplete around Ti and Pb atoms (green region). The charge distribution at the interfaces could form an internal electric field to affect the charge transmission properties of the solar cells. Thus, the more stable PbI$_2$/TiO$_2$ interfaces are supposed to cause a stronger internal electric field and make the electron-hole pairs separate more easily at the interfaces. Our calculations of the stability and bonding characteristics of TiO$_2$/perovskite interfaces consistwell with previous results, which verify the accuracy of the interface model and make our further investigation more reasonable.
3.2 The electronic characteristics of rutile $\text{CH}_3\text{NH}_3\text{PbI}_3$ interfaces by considering the defect effects

The electronic properties at the interfaces are closely related to the electronic transmission at the interfaces. To understand the defect effects on the electrical properties of rutile $\text{CH}_3\text{NH}_3\text{PbI}_3$ interfaces, we first resort to the partial density of states (PDOSs) of the clean interfaces as depicted from Figure 3, the conduction band minimum (CBM) of TiO$_2$ at PbI$_2$/TiO$_2$ interfaces are all significantly lower than that of perovskites. Because with a proper band gap, perovskites always act as the light absorption layer, electrons should be excited from the top of the valence band maximum (VBM) ($\text{I}_p$ and Pb-$s$ orbitals) of perovskites to the CBM of perovskites (Pb-$p$ orbitals) and then transfer from the conduction bands of the perovskites to the conduction bands of TiO$_2$ ($\text{Ti}_d$ orbitals). It also clearly shows that MA molecules have little effect on CBM and VBM at the interfaces and almost no participation in electronic transmission. At the same time, we obtain that the band gap of perovskite is 1.74 eV. To further understand the characteristics of the electronic transmission at the interfaces, the defect effects will be discussed in the following.

![Figure 3. Partial density of states (PDOSs) for the upper and lower two-layer atoms at the PbI$_2$/TiO$_2$ interfaces.](image)

Defects are more likely to occur at the interfaces, and the produced defects are likely to affect the electron transport properties at the interfaces. Some I vacancies, I interstitials and Pb vacancies in perovskites seem inevitable by the previous studies. Ho et al. have also indicated that there are common O vacancies in TiO$_2$[16]. Therefore, we have studied the formation of four typical defects (V$_I$, I$_i$, V$_{\text{Pb}}$, V$_{\text{Ti}}$) that may occur at the interfaces and analyzed their influence on the electron transport properties at the interfaces. The formula for calculating defect formation energy ($E_f$) is shown in the following Eq.2.

$$E_f = E_d - E_{sc} \pm \mu_c \quad (2)$$

$E_d$ and $E_{sc}$ represent the total energies of the system with and without defects, respectively. $\mu_c$ is the chemical potential of element substance ( $\mu_I = -1.78$eV, $\mu_O = -4.47$eV, $\mu_{\text{Pb}} = -4.08$eV).

| defect | V$_I$ | I$_i$ | V$_O$ | V$_{\text{Pb}}$ |
|--------|-------|-------|-------|---------------|
| Formation energy (eV) | 1.58  | 0.31  | 2.66  | 2.80          |

We remove an atom (I, O, Pb) from the optimized PbI$_2$/TiO$_2$ interface to produce vacancy defects or added an atom (I) to the interface to produce interstitial defects. It can be seen from the Table 3 that the most easily formed defects at the interface are the I interstitial and I vacancy, which have small formation
energies of 0.31 and 1.58 eV, respectively. These results are consistent with the previous research. Also, for the defect of oxygen vacancy, the formation energy at the interface we calculated is 2.66 eV, which matches well with the previous calculations. Comparatively, the Pb vacancy is hard to form with a larger formation energy of 2.80 eV. After the structural relaxation by using the PBE functional, we calculate the electronic structure of the defect systems with the precise HSE06 functional. Figure 4 shows the PDOSs of these four defect systems. Then, the effect of defects on the electron transport properties at the interfaces can be understood.

![Figure 4. PDOSs for the upper and lower two-layer atoms at the PbI₂/TiO₂ interfaces with different defects: (a) I vacancy; (b) I interstitial; (c) O vacancy; (d) Pb vacancy.](image)

As shown in Figure 4(a), we can see the formation of V_I at the interfaces could lower the CBM of perovskites by shifting the position of Pb-p orbitals, which might reduce the PCE of PSCs. This phenomenon has also been observed in the previous research. For I_i, it has little effect on the band gap, VBM and CBM. It means a small amount of I interstitial defects at the interfaces might not affect the performance of the solar cells (Figure 4(b)). However, with the accumulation of I interstitial at the interfaces, the effect could not be ignored. The previous study has reported that the accumulation of I interstitial could lead to the increase of different ionic traps or capture of carriers, and then decrease the PCE of PSCs. Similarly, the effects of V_O on the band gap, CBM and VBM are also inconspicuous (Figure 4(c)). As shown by Zhang et al.'s research, oxygen vacancy in TiO₂ at high concentrations could obviously reduce the capacity of electron extraction and transfer for PSCs[17]. However, the V_Pb at the interfaces produces a distinctive defect level (I-p) at E = 2.1 eV (Figure 4(d)). The shallow defect level locates just below the CBM of TiO₂, which could affect the transmission of electrons from perovskites to TiO₂ in the conduction band. We can attribute this influence to the change of the bond characteristics at the interfaces. As Pb atoms are bonded to I atoms at the interfaces, the remove of Pb atoms might cause the dangling bonds of I atoms. Thus, the produced defect V_Pb could be detrimental to the performance of the solar cells.

4. Conclusion
In brief, we have studied the stability and bonding characteristics of PbI₂/TiO₂ interfaces by using the first-principles method. The results have confirmed that the PbI₂/TiO₂ interfaces have a high interfacial binding energy of -0.93 J/m² where the Ti-I and Pb-O bonds could form. Furthermore, the electron transport at the interfaces has been analyzed by the partial density of states by comparing the clean interfaces and interfaces with different defects. In the clean PbI₂/TiO₂ interfaces, a stronger internal electric field is produced which might make the electron-hole pairs separate more easily at the interfaces. Also, it is found that common defects V_I and I_I are relatively easy to form at the interfaces. Some defects at low concentrations might have little effect on the electron transport at the interfaces, while they are
harmful only when the concentration increases. However, $V_{pb}$ with a high formation energy could adversely affect the electron transmission even at low concentrations. These result helps us to have a deeper understanding for the effects of different defects on the interfacial electron transport. On this basis, we will further explore other factors that might affect the electron transport and environmental instability at the perovskite/ETL interface, such as stress caused by lattice mismatch, temperature and ultraviolet rays.

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