Modeling of Halide Perovskite/Ti$_3$C$_2$T$_X$ MXenes Solar Cells

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Abstract—**Solar cells based on metal halide Perovskites have gained a key role in the field of photovoltaics due to their high efficiencies and low production costs. Still, there is considerable effort invested in tuning the perovskite crystal morphology and interface properties, in order to further improve the device performance. Among the solutions proposed so far, MXenes have recently turned into focus for their possibility of being incorporated within the perovskite and carrier transport layers, resulting in an important improvement of the cell efficiency. In this work, we present device simulations of Perovskite/MXene solar cells, where modeling of the interface energy alignments has been based on measurement data and ab initio calculations.**

I. Introduction

Among all third generation solar cells, hybrid organic/inorganic lead halide perovskite based devices are showing since several years the best performance in terms of power conversion efficiency (PCE). In fact, their record efficiency has surpassed that of other thin film solar technologies [1]. Nevertheless, perovskite solar cells (PSC) have still room for improvement, and effort is put in particular into optimization of crystal morphology and interface properties [2].

Recently, transition metal carbides, nitrides and carbonitrides (MXenes) have found to be suitable materials, which added in small amount into the perovskite or the transport layers can be used to engineer the work function (WF) of the different layers in order to improve the energy alignments [3]. MXenes have a general chemical formula of M$_{n+1}$X$_n$T$_x$ with $n = 1$–3, where M represents a transition metal, X a carbon or nitrogen, and T$_x$ indicates the surface terminations like –OH, =O, and –F. The large number of degrees of freedom in the chemical composition of these materials allows for a fine tuning of their electronic properties, in particular the WF.

In this work, we study the modification in performance of mixed cation perovskite solar cells due to addition of small amounts ($\sim$0.03%) of Ti$_3$C$_2$T$_x$ MXene into the perovskite or the electron transport layer. By proper modeling of the effect of the MXene additive, we are able to reproduce the experimental trends in open circuit voltage, short circuit current and fill factor.

II. Modeling approach and results

The interaction between MXenes and perovskite has been studied by first-principles calculations in the framework of density functional theory (DFT). Here, we consider the interface between a CH$_3$NH$_3$PbI$_3$ layer in cubic phase and a Ti$_3$C$_2$T$_x$ MXene layer, with the T$_x$ functional group being F, O or OH. We analyzed in particular the electrostatic potential profile along the material stack and the electronic band structure of the system, as depicted in Fig. 1. The functionalization of the MXene surface is found to play a crucial role for the electronic properties of the combined MXene/perovskite system. Most significantly, the presence of the Ti$_3$C$_2$T$_x$ leads to a strong modification of the perovskite WF, depending on the surface termination.
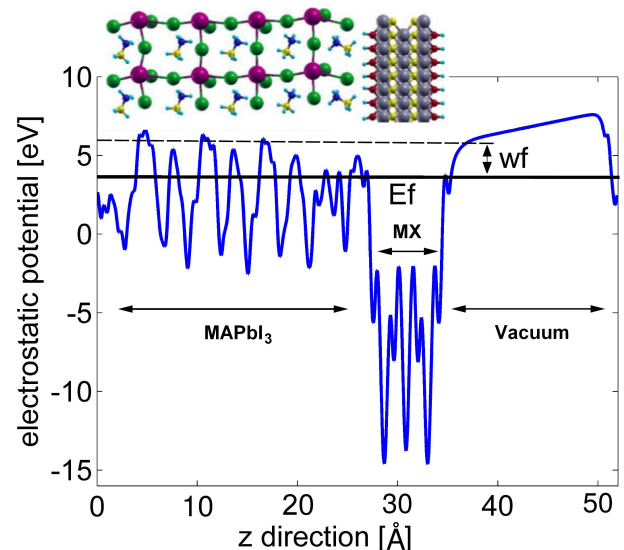

Fig. 1. Plane averaged electrostatic potential plotted along the direction perpendicular to the MAPbI$_3$/Ti$_3$C$_2$(OH)$_2$ interface. The thick line indicates the Fermi energy. The WF of the MAPbI$_3$/MX interface is given by the difference between the dashed line and the Fermi energy.

The OH group in particular causes a strong reduction of the work function due to a charge transfer induced interface dipole, which modifies the energy alignment between perovskite and the transport layers. These calculations confirm the conclusions drawn from UPS measurements.

Based on these results we performed drift-diffusion (DD)[4] simulations for a series of devices, where the MXenes have been added in the perovskite layer, and in the TiO$_2$ transport layer as well. We start our investigation modelling a

reference solar cell made by the FTO/TiO$_2$/Perovskite/Spiro-OMeTAD/Au stack, where the 550 nm thick perovskite absorbing layer has band edges placed at E$_C$ = -3.9 eV and E$_V$ = -5.5 eV. The charge carrier generation profile is calculated from the FTO contact using a Lambert-Beer model, using a typical perovskite absorption spectrum[5]. Recombination is modelled by accounting losses at both transport-layer/perovskite interfaces, and including in the bulk radiative recombination and trap-assisted contributions (Shockley-Read-Hall). We set for the radiative recombination a rate constant B$_{rad}$ = 3×10^{-9} cm^{3}s^{-1}, and for SRH a characteristic lifetime of τ_{SRH} = 2×10^{-8} s.

In order to investigate the impact of MXene inclusion on the solar cell performance we model two further devices. In the first, the MXenes are only added to perovskite (type A), whereas in the second they are added to both the TiO$_2$ and perovskite (type B). According to UPS results, we model the WF reduction by applying a rigid upshift of the band edges by 0.35 eV of the perovskite for type A, and a further upshift of 50 meV of the TiO$_2$ for type B. According to absorbance measurements, we also increase the charge carrier generation by 3% and 4.5% in the perovskite layer of type A and B, respectively. In addition, we assume the MXenes inclusion slightly increases the amount of bulk defects, which we model by setting for both types τ_{SRH} = 1.5×10^{-8} s. All other parameters used for simulations have been left unchanged.
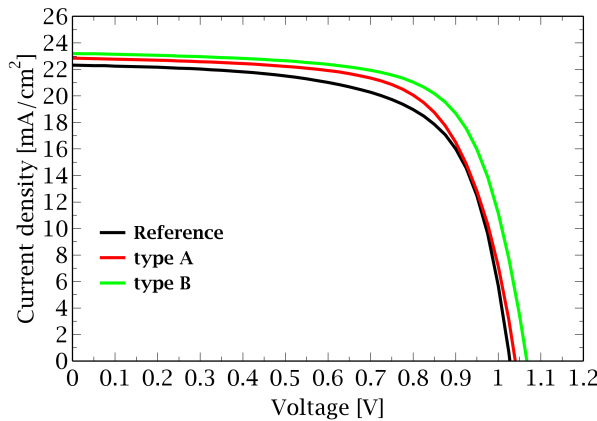

Fig. 2. J-V characteristics calculated with DD simulations for the reference device and the modified structure A and B with the MXenes additive.

Figure 2 shows the comparison between J-V characteristics obtained calculating the charge transport for the reference structure and modified type A and B devices. From calculations we can deduce that the significant increase of the solar cell performance is due to two different mechanisms. First, the upward energy shift of perovskite (in type A) and of TiO$_2$ as well (in type B) improves the band alignment at TiO$_2$/Perovskite interface, and mainly leads to an increase in the open-circuit voltage (V$_{OC}$). Moreover, both interface recombinations and effective bulk losses are reduced. Second, in agreement with experimental results, the gradual increase of the short-circuit current density (J$_{SC}$) is due to a slight increase of the effective absorption within the perovskite layer.

From performance parameters summarized in Fig. 3 we observe the beneficial effect of the MXenes inclusion in both the absorbing and electron transport layer.
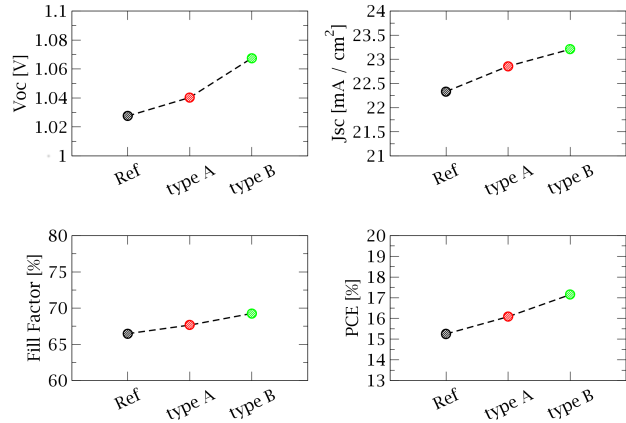

Fig. 3. Summary of main performance parameters obtained for all devices studied.

The most important result is definitely the improvement of the power conversion efficiency (PCE), which increases from the 15.25% of the reference device up to 17.15% in type B structure. As obtained by DFT and DD calculations, we conclude that the proper tuning of the absorption and transport layers' WF by MXenes inclusion can be exploited to significantly improve the performance of PSC.

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