Interfacial modification of perovskite solar cells via Cs_2CO_3 : Computational and experimental approach

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Abstract

Interfacial materials in perovskite solar cells (PSCs) between the absorber layer and charge selective layers are stimulants to boost performance and long-term stability. Incorporation of a low-temperature processed passivating agent at electron selective layer/perovskite interface can enhance the performance of PSCs, however, the interface at $\text{SnO}_2/(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ suffers from surface phenomena that retard the overall performance of the PSCs. By adopting a synergistic approach, drift-diffusion simulation, and experimental validation we unravel the interaction of the passivation layer at electron selective layer/perovskite. Firstly, we elucidated the impact of defect density (N_t) at electron selective layer/perovskite and the conduction band of SnO_2 using drift-diffusion simulation to yield a power conversion efficiency of 23.18 %. Secondly, we validate the simulation trend experimentally, by depositing the Cs_2CO_3 passivation layer on the top of the electron selective layer. The impact of Cs_2CO_3 on electro-optical properties, charge collection, and recombination rate at the interfaces of PSCs was unraveled. The PSC fabricated with Cs_2CO_3 treatment achieves a higher open-circuit voltage, $V_{oc} \sim 1090$ mV. Our findings put

forward a combinatorial protocol of drift-diffusion simulation and experimental studies to address the interfacial issues in PSCs.

Keywords: Perovskite Solar Cell, Interface engineering, SnO₂, Cs₂CO₃, Drift-diffusion Simulation

Introduction

The simplicity and versatility of perovskite solar cells (PSCs) have attracted interest in the photovoltaic community and reached an efficiency of 25.5 % (NREL,2021). PSCs display excellent electro-optical properties (Herz, 2016; Leijtens et al., 2020; Miyata et al., n.d.; Wang et al., 2016), however, the interface recombination remains as a barrier in PSCs to attain Shockley Queisser limit and long-term stability enhancement. Typically, a PSC structure consists of; perovskite as light absorber sandwiched between electron transport layer (ETL) and hole transport layer (HTL) creating two main interfaces, regardless of *n-i-p* or *p-i-n* type architect. Until now the *n-i-p* type structure shows high device performance, and the role of ETL is efficient transport of charges to the electrodes. SnO₂ is being investigated as a promising ETL for PSCs not only due to its low-temperature process and UV light stability as compared with TiO₂ or ZnO (Zhou et al., 2019) but also higher mobility. Diverse strategies have been applied at SnO₂/perovskite interface using additives {graphene quantum dots, (GQDs), EDTA)}, dopants (Li⁺, K⁺, Mg⁺, and Al⁺³, etc.) as well as bilayer strategies (SnO₂/TiO₂, SnO₂/ZnO or SnO₂/QD-SnO₂) to optimize the performance of PSCs by decreasing the interface recombination and to boost the optoelectronic properties of SnO₂ (Nair et al., 2020; Park et al., 2016; Thomas and Skariah, 2015; Yang et al., 2018; Zhu et al., 2019, 2014). Unraveling a synergetic approach that enhances the interface charges and, quality of the perovskite layer will be paramount. The incorporation of Cesium salts (CsX, here X is halide) is an effective methodology, as CsX can enhance the surface quality of SnO₂ and a trivial amount of CsX can diffuse into the perovskite layer (Pang et al., 2021; Saliba et al., 2016a).

The Cesium carbonate, (Cs_2CO_3) was reported to reduce the work function of SnO_2 in an organic solar cells (Shen et al., 2020; Yoon et al., 2019; Zong et al., 2019). Recently, Cs_2CO_3 was used as a source of Cs element for the perovskite layer to enhance the performance and stability of PSCs (Yavari et al., 2021). Theoretical simulations allow a faster analysis of conditions and combinations, considerably reducing the amount of effort required to identify potential candidates in terms of materials and methods, and increasing the analysis capabilities. Device model simulation is a macroscopic computer-assisted technique used to simulate thin-film solar cells (short-circuit current density, open-circuit voltage, fill factor, and efficiency). The device kinetics can be explained by charge carrier generation, transportation, recombination, and collection related to the electrical characterization that is governed by the semiconductor equations (including Poisson, drift-diffusion, and continuity equations) (Li et al., 2020; Raoui et al., 2021b). Thus, the modeling and simulation studies are attractive for the PSCs community to accelerate the development. By employing drift-diffusion simulation, we have detailed the behavior of $\text{SnO}_2/(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ interface; and noted that a spike structure at ETL/perovskite can boost the performance. To experimentally validate this hypothesis, we placed Cs_2CO_3 thin layer in between $\text{SnO}_2/(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ to form spike structure (Raoui et al., 2021a).

Cs_2CO_3 as an interlayer between SnO_2 and the perovskite layer was deposited through the spin-coating method. To elucidate the impact of Cs_2CO_3 on the performance of PSCs, we run drift-diffusion simulation in the configuration of, FTO/ SnO_2 /interface layer 1 (IL1)/ $(\text{FAPbI}_3)_{0.85}\text{MAPbBr}_3)_{0.15}$ /interface layer2(IL2)/Spiro-OMeTAD/Au to illustrate the trap density reduction at IL1 and the energy level of SnO_2 . Firstly, we noted that reducing the defect density at IL1 can boost the PSCs performance, while the drift-diffusion simulation suggests optimization of the electron affinity of SnO_2 for efficient extraction of free charges. Secondly,

experimental results using Cs_2CO_3 as an interlayer ratify the drift-diffusion simulation results and validate performance and stability enhancement.

Computational Studies

The simulations were performed using the one-dimensional Solar cell capacitance simulator SCAPS 3.3.07 software (Raoui et al., 2019) based on the Poisson equation and the continuity equations for electrons and holes (supporting info).

Results and discussion

Control devices: Experimental & drift-diffusion simulation

The simulated model and experiment with the configuration of FTO/ SnO_2 /(IL1)/(FAPbI₃)_{0.85}MAPbBr₃)_{0.15} / (IL2)/ Spiro-OMeTAD /Au pave way for further optimization as illustrated in Fig. 1a-b. The input parameters used to perform the simulation are summarized in Table S1.

Fig. 1: a) Schematic diagram for the device structure adapted to experimental investigation, b) the energy level of different layers used in drift-diffusion simulation c) J - V curves, and d) theoretical and experimental EQE with integrated J_{sc} .

As illustrated in Fig. 1c, the simulated device is quite close to the experimental results, which suggests the suitability of our model device for further optimization. From the simulated EQE (Fig. 1d) we can observe that the absorption and excitation of free charges inside the PSC are fine, but we speculate that the low defect density at the ETL/perovskite leads to poor extraction of electrons, which maximize the possibility of recombination. To confirm our hypothesis, in the next section we focused on the effect of defect density at ETL/perovskite.

Interface recombination

To shed light on the interfaces recombination, a modified Shockley-Red-Hall model that describes the effect of defect density is adapted as following (Kemp et al., 2013; Wilhelm et al., 2011):

$$R_{IL} = \frac{n_{IL}p_{IL}-n_i^2}{S_n^{-1}(n_{IL}+n)+S_p^{-1}(p_{IL}+p)} \quad (1)$$

R_{IL} is the total interface recombination, where (n_{IL} , p_{IL}) are the electron and hole concentration at interfaces. The terms n and p are related to the emission rate from the defect energy state to the corresponding band edges (E_c , E_v) at interfaces. S_n , S_p are the hole and electron interface recombination velocities which are related to the defect density (N_t), capture cross-area of trap for electron as well as hole and the thermal velocity following the equation (1):

$$S_{n,p} = N_t \sigma_{n,p} v_{th} \quad (2)$$

For highly doped selective layers, the interface recombination rate reduces to $R_{IL} = S_p$

The interface quality is sensitive to the trap density between the perovskite and selective layers, which can undermine the performance and stability of PSCs. Thus, the effect of defect density at the ETL/perovskite (IL1) on the performance of PSCs was investigated, for this, we kept thermal velocity and capture cross-area of trap for electron and holes constant (Fig. 2).

Expectedly, the defect density at IL1 has a significant effect to boost the performance of PSCs, as the N_t decreased below $1\text{E}17\text{ cm}^{-3}$, the photovoltaic parameters increase firstly, and then saturated when the N_t reaches a value of $1\text{E}13\text{ cm}^{-3}$, compared to the controlled PSC, upgraded performances yielded a PCE~23.18 %, with a V_{oc} ~1190 mV, J_{sc} ~24.90 mA/cm² and FF~77.71 %. The improvement can be ascribed due to the reduction of trap density at ETL/perovskite, which will allow efficient collection of free charges by reducing the recombination rate (Fig. 2d).

Fig. 2: The theoretical impact of defect density on a) photovoltaic parameters), b) $J-V$ curves, c) EQE, and d) total recombination rate at ETL/perovskite.

Experimentally, the Cs_2CO_3 has been deposited as an interlayer to imitate the behavior of simulation results. The addition of Csx would add a beneficial effect on improving the efficiency, reproducibility, and stability of PSCs (Saliba et al., 2016b). We optimized the performance of PSCs by varying the concentrations of Cs_2CO_3 and noted 0.5 mg/ml as an optimum value. Thus, all characterization will be based on this optimum concentration. Crystallography data of perovskite are investigated using X-ray diffraction (XRD) patterns (Fig. 3a), which display perovskite without/with Cs_2CO_3 showed significant changes. The intensity of the peak at 12.7° is

decreased with Cs_2CO_3 treatment, this peak is characteristic of residual PbI_2 as well as a slight decrease of the peak at 11.5° which corresponds to the δ -phase of FAPbI_3 (Cho et al., 2017). The photoactive black phase of the perovskite layer is likely to be present by the addition of Cs (Erazo et al., 2020; Saliba et al., 2016b; Yavari et al., 2021). The absorption spectra are similar in both cases as illustrated in (Fig. 3b). The microstructure of SnO_2 and perovskite layer without/with Cs_2CO_3 were investigated using scanning electron microscopy (SEM) images (Fig. 3f). SEM image shows that SnO_2 grown on c- TiO_2 displays poor surface quality, the presence of pinholes can increase the recombination at the interfaces, in contrast to the microstructure achieved by the surface of Cs_2CO_3 display its ability to fill the surface pinholes of SnO_2 . The perovskite grown on $\text{SnO}_2/\text{Cs}_2\text{CO}_3$ has large and smoother grains, which minimize the defect density and improve the charges transfer, suggesting its role in perovskite crystallization (Akin, 2019):

Fig. 3: a) X-ray diffraction patterns of control perovskite film (black) and perovskite growth on Cs_2CO_3 , b) UV-vis absorption spectra of perovskite without and with 0.5 mg/ml of Cs_2CO_3 . SEM images of c) FTO, d) FTO/c- TiO_2 /SnO₂, e) FTO/c- TiO_2 /SnO₂/perovskite, f) FTO/c- TiO_2 /SnO₂/perovskite/0.5 mg/ml of Cs_2CO_3 .

Photovoltaic performance

Fig. 4: Photovoltaic characteristics with 0.5 mg/ml of Cs_2CO_3 (CsC) and without treatment, a) $J-V$ curves, b) EQE, c) the Mott-Schottky plot, d) Nyquist plot, e) $C-V$ curves spectra, and f) steady-state power output.

Fig. 4a depicts the $J-V$ curves with different concentrations of Cs_2CO_3 , the performance of the device is improved to a PCE~17.83 %, V_{oc} ~1090 mV, J_{sc} ~23.31 mA/cm², and FF~69.67 % by varying the rate of Cs_2CO_3 from 0 – 1 mg/mL yielding an optimal concentration of 0.5 mg/mL.

Furthermore, the Cs_2CO_3 reduces the trap state of SnO_2 in organic solar cells (Yoon et al., 2019). Cs_2CO_3 can reduce the recombination rate at SnO_2 /perovskite, significantly affecting the PSCs performance with a stagnation point that declines the performance thereafter.

To quantify the impact of Cs_2CO_3 on the performance of PSCs, we carried out the space charge limited current (SCLC) measurements for electron-only devices with the structure of FTO/c- TiO_2 / SnO_2 (with and without Cs_2CO_3) / $(\text{FAPbI}_3)_{0.85}\text{MAPbBr}_3)_{0.15}$ / PCBM /Au. The trap density (N_T) was calculated using the equation $\left(N_T = \frac{2\epsilon\epsilon_0 V_{TFL}}{qL^2}\right)$. The trap-filled limit voltage (V_{TFL}) is 0.07 V and 0.09 V for perovskite with and without Cs_2CO_3 , respectively

The trap-filled limit voltage (V_{TFL}) is 0.07 V and 0.09 V for perovskite with and without Cs_2CO_3 , respectively. The N_T calculated are $1.41\text{E}+16 \text{ cm}^{-3}$ and $1.10\text{E}+16 \text{ cm}^{-3}$ for the controlled device and with Cs_2CO_3 . The PSCs with Cs_2CO_3 show low defect density, which we ascribe to the passivation of interfacial defects at the ETL/perovskite.

To estimate the improvement of PCE with Cs_2CO_3 , the built-in potential (V_{bi}) and depletion layer width (W) at perovskite/ETL are performed using Mott-Schottky analysis. The Mott-Schottky plot (Fig. 4d) of the control PSC and with Cs_2CO_3 at 10KHz is presented; the response of forward bias voltage near or above the built-in voltage corresponds to the capacitance (C) caused by electrode polarization and charge accumulation at the interfaces (Almora et al., 2016). The following equation describes the C related to previous parameters (Gelderman et al., 2007; Hemasiri et al., 2020; Khan et al., 2019):

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 A^2 qN} \left[V - V_{bi} - \frac{k_b T}{q} \right] \quad (3)$$

Where ϵ is the relative dielectric constant of the perovskite layer, ϵ_0 is the vacuum permittivity, and A is the active area. The other parameters are described in the previous sections. The built-in potential was found to be similar in both PSCs, $\sim 910\text{mV}$. Thus, using the slope value, the depletion

width $\left(W = \sqrt{\frac{2\epsilon\epsilon_0 V_{bi}}{qN}}\right)$ of the modified PSC (0.5 mg/ml Cs_2CO_3) showed 249 nm compared to 247 nm for the control PSC, suggesting the charge separation improvement and reduction in recombination at perovskite/ETL interface. In the Nyquist plot (Fig. 4e) of with and without Cs_2CO_3 , the arc at the low-frequency region is associated with the recombination resistance (R_{rec}), higher R_{rec} values indicate less recombination and efficient separation of free charges at the interfaces (Wang et al., 2017), this is following the above results.

The effect of conduction band offset

The conduction band offset (CBO) is the difference between the electron affinity of ETL and perovskite, ($\text{CBO} = \chi_{\text{ETL}} - \chi_{\text{perovskite}}$). Theoretically, the energy level between ETL and perovskite is a crucial parameter that can control the collection of free charges toward the back contact (FTO) in terms of spike and cliff structure as we demonstrated in our previous work. The optimized spike structure, i.e, +CBO has a positive effect on improving the performance of PSCs by minimizing the recombination rate at the ETL/perovskite (Raoui et al., 2021a). (Fig. S2) shows the range of electron affinity adopted to study the effect of CBO on the PSCs performance. We can speculate that the decline of the performance at an optimal concentration of Cs_2CO_3 (0.5mg/ ml) is a result of the energy level tuning at ETL/perovskite. Thus, starting from the concept of drift-diffusion simulation, we varied the electron affinity of SnO_2 from 3.75 to 4.15 eV (i.e, CBO from 0 to 0.4 eV), in parallel with the variation of defect density at IL1 (Fig. 5). From the previous results, the $N_t = 1\text{E}13 \text{ cm}^{-3}$ was found to be the optimal value at IL1. However, on decreasing the electron affinity of SnO_2 the improved performance was noted till an optimum value (CBO = 0.35 eV) which corresponds to $\chi_{\text{ETL}} = 3.8 \text{ eV}$ and then depending on the value of N_t , it saturates or decreases. Which can simulate the behavior of experiment results with optimal concentration (0.5 mg/mL).

This signals the synergetic role of Cs_2CO_3 as a passivating layer at ETL/perovskite and to tune the ETL energy level. Unraveling the impact of interfacial modification at ETL/perovskite is key to optimize the optoelectronic proprieties of perovskite and on the energy level of ETL to decipher interface issues in PSCs to push its performance.

Fig. 5: (a-a') The effect of the electron affinity of SnO_2 on the performance of PSC using drift-diffusion simulation.

Conclusion

To conclude, interface engineering is a key to improve the performance of perovskite solar cells. The synergy between experimental and theoretical investigation is vital to understand different phenomena behind the device fabrication. We demonstrated the benefits of Cs_2CO_3 as an interfacial passivating layer at ETL/perovskite to boost the efficiency of perovskite solar cells by reducing the recombination rate at the interface. Further, the drift-diffusion simulation is introduced to unravel the impact of reducing the defect density at ETL/perovskite. Experimentally, we noted that 0.5 mg/ml of Cs_2CO_3 is the optimum concentration and it yielded an efficiency of

17.83 %, while we simulated efficiency of 23.18 % by optimizing the defect density at ETL/perovskite. These results help to provide a useful strategy to fabricate and model efficient perovskite solar cells.

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