

THERMAL STABILITY ENHANCEMENT OF PLANAR PEROVSKITE SOLAR CELLS VIA DYE SENSITIZATION OF TITANIA COMPACT LAYER

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ABSTRACT

Herein, we introduce the sensitization of the titania compact layer via the triphenylamine-based metal-free organic (E)-3-(5-(4-(bis(2',4'-dibutoxy-[1,1'-biphenyl]-4yl) amino) phenyl) thiophen-2-yl)-2-cyanoacrylic acid (D35) dye, as a totally novel strategy to modify the titania compact layer/perovskite interface and improve the stability of planar Perovskite Solar Cells (PSCs). For this purpose, we fabricated PSCs with the following configuration: FTO/TiO₂/CH₃NH₃PbI₃/spiro-OMeTAD/Ag as the control device and FTO/TiO₂/D35/CH₃NH₃PbI₃/spiro-OMeTAD/Ag as the sensitized one, and subjected them at thermal stress at 100°C. The dye-sensitized devices showed an obvious enhancement in terms of thermal stability, since after 60 min of annealing at 100°C, the spectroscopic properties of the perovskite films grown upon TiO₂/D35 remained practically intact, while the perovskite layer of the control device, began to deteriorate and extended lead iodide areas appeared as a signal of severe degradation. As a result, the photovoltaic performance of the reference PSCs was severely decreased, contrary to the D35-sensitized ones that preserved 70% of their initial efficiency.

INTRODUCTION

Perovskite solar cells (PSCs) of general formula ABX₃ (where A is an organic/inorganic cation, B is a metal cation, and X is a halide anion) are characterized by low-cost fabrication methods[1,2] and high power conversion efficiencies (PCEs) which raised from 3.8% to 24.2% in only a few years of development[3-8]. The chemical and environmental instability of PSCs is one of the main reasons that prevent them from broad commercialization, thus fabrication of stable perovskite crystals is a giant step towards implementation of large scale applications. In this context, stability against thermal strain is one of the tests that PSCs should successfully undergo, since it is well established that photovoltaic protocols aspiring to enter into the production line, should be stable when operating at 80°C under 1 sun illumination (100 mWcm⁻²) for more than 1000h [9-14]. Therefore, further investigation and improvement upon PSCs is required, in order to develop highly performing devices for practical applications [15-16].

EXPERIMENTAL PART

FABRICATION OF PEROVSKITE SOLAR CELLS

The PSCs were fabricated by depositing the successive layers upon 20mm×15mm Fluorine Tin Oxide conductive substrates (FTO, Aldrich, 7 Ω/□). The FTO were patterned with a 2molL⁻¹ aqueous HCl solution in combination with zinc powder and were carefully cleaned and sonicated into a bath with Triton-X, acetone, 2-propanol, and UV ozone in 15 min cycles. The TiO₂ Electron Transporting Layer (ETL) was spin-coated at 2000rpm for 60s from a mildly acidic solution of

titanium (IV) isopropoxide (Aldrich, 97%) in ethanol. The films obtained were annealed for 45 min at 500 °C under a 5 °C min⁻¹ temperature ramp rate. To modify the films with the D35 dye, we immersed them overnight into a 4 mol L⁻¹ ethanolic solution. Subsequently, we sonicated them for 10 min in ethanol to discard the dye molecules not chemically bonded with the titania substrate and the films color turned to orange. Then, the films were dried under Ar flux and transferred into an Ar-filled glovebox for the further experimental procedures. The CH₃NH₃PbI₃ layer was deposited by spin-coating in an one-step procedure from a perovskite solution in anhydrous N,N-dimethylformamide, containing a 40 wt % methylammonium iodide (Dyesol) along with lead acetate trihydrate (PbAc₂·3H₂O, 99.999% trace metals basis, Aldrich) in a 3:1 molar ratio. A small amount of hypophosphorous acid (50% w/w, aqueous solution, Alfa Aesar) was also added to the perovskite solution so that the final molar ratio of HPA:PbAc was 1:4. The procedure was carried out at 2000 rpm for 45 s. The films were left to dry at room temperature for 10 min and were annealed at 100 °C for 5 min. Finally, a 7 wt % Spiro-MeOTAD (Borun Chemical) solution in chlorobenzene was deposited as the hole transport layer, containing additives of lithium bis(trifluoromethanesulfonyl)imide lithium salt (≥99%, Aldrich) in acetonitrile and 4-tert-butylpyridine (96%, Aldrich). The deposition was realized at 3000 rpm for 30 s. Finally, the devices were transferred outside the glovebox, and six 100 nm thick silver electrodes were thermally evaporated under vacuum of 10⁻⁶ Torr, at a rate of 1 Ås⁻¹. The final structure of the devices is shown in Figure 1.

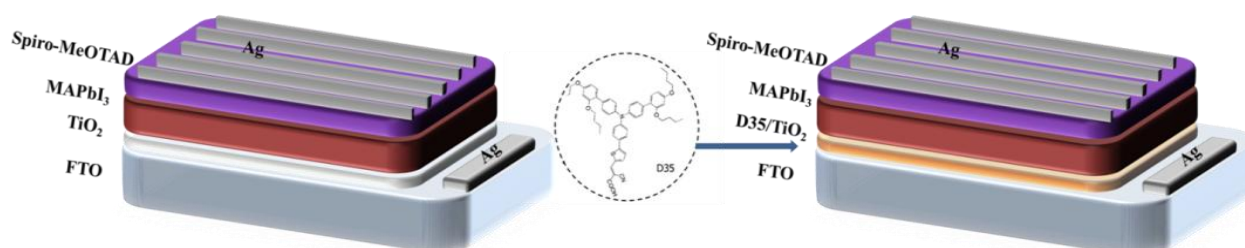


Figure 1. The structure of the PSCs fabricated without D35 (left) and by adding D35 in the compact TiO₂ layer (right)

RESULTS AND DISCUSSION

UV-vis absorbance measurements were carried out for both the control and the D35-modified device after 30 and 60 min of thermal stress at 100°C. It is obvious that the thermal annealing decreased the absorption of both devices, however less in the case of the modified devices as

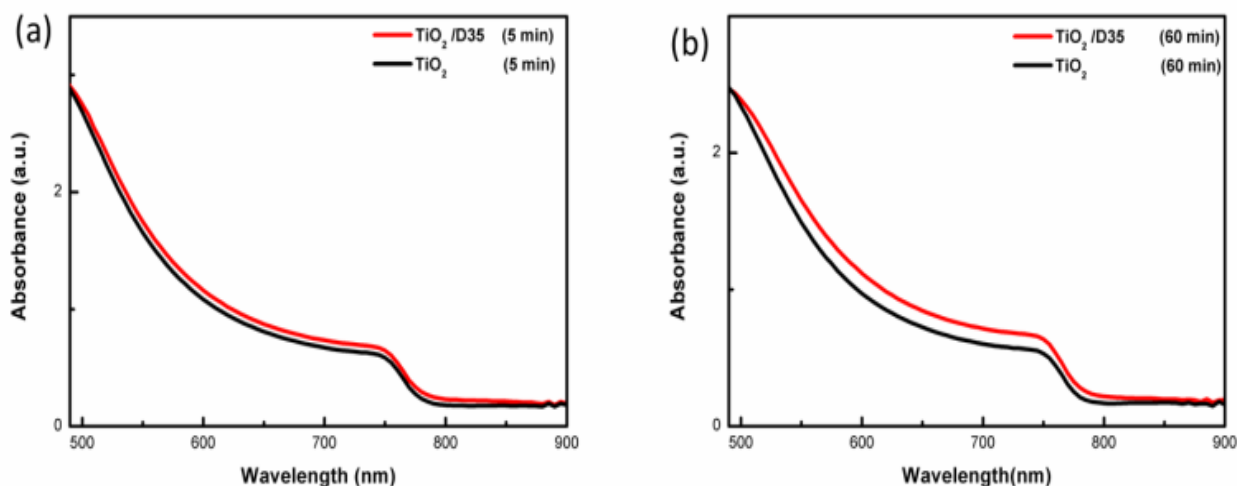


Figure 2. UV-vis absorption spectra for devices with and without D35 after (a) 5 minutes of annealing as reference case and (b) after 60 minutes as a stress test case.

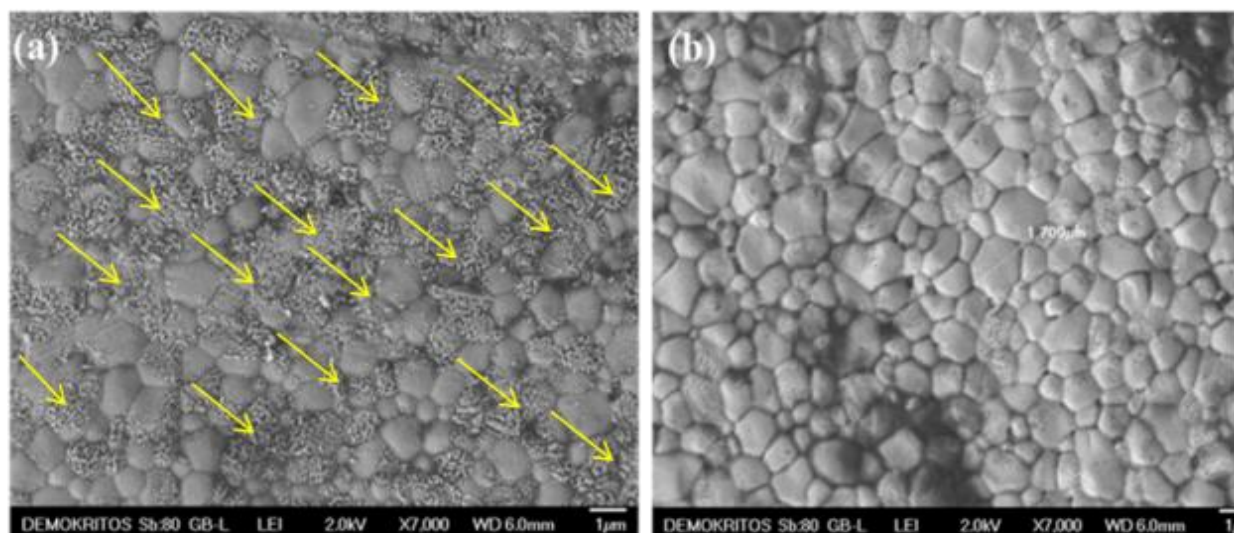


Figure 3. SEM images for samples without (a) and with (b) D35 after 60 minutes of annealing at 100°C (arrows refers to PbI_2 areas)

shown in Figure 2. In order to corroborate the degradation of the perovskite crystals, scanning electron microscopy (SEM) images were taken from perovskite films grown on TiO_2 and D35/ TiO_2 layers. The images were taken after 60 minutes of thermal stress at 100°C (Figure 3) in ambient conditions. It is clear that the perovskite crystals started to degrade and lead iodide appeared in the control samples, while in the sensitized ones the perovskite crystals are preserved in a better condition because the D35 acts as a versatile shield layer, enhancing the perovskite durability against moisture and heat.

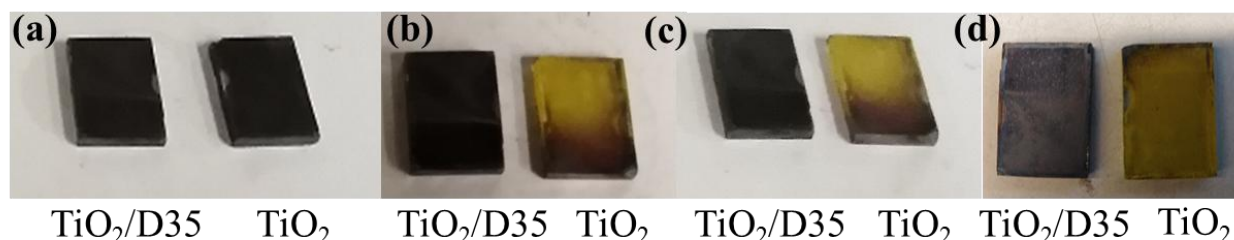


Figure 4. Images of TiO_2 /D35 and TiO_2 films upon perovskite layers thermally stressed at 100°C on air for (a) 5 minutes (b) 95 minutes (c) 120 minutes and (d) 185 minutes

Afterwards, prolonged thermal stress at 100°C on air (Figure 4) was performed for perovskite layers upon TiO_2 and TiO_2 /D35 films. The perovskite layer on the neat TiO_2 film started turning to yellow due to lead iodide appearance after 95 minutes of annealing, a phenomenon more intense after 120 minutes. On the other hand, the perovskite layer on the TiO_2 /D35 film remained dark confirming that the layer still consists of perovskite crystals. The test went on till the perovskite//D35 TiO_2 film turned completely yellow, indicating the dominance of lead iodide after 185 minutes of heat at 100°C. On the other hand, the control samples preserved their macroscopical dark view, indicating a better structural behavior against the heat strain tests.

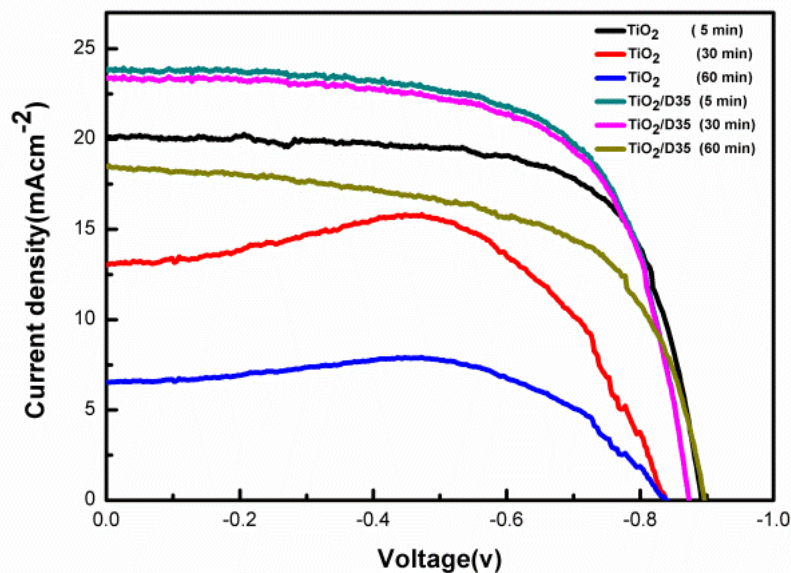


Figure 5. J-V curves for control and sensitized devices after 30 and 60 minutes of annealing

J-V curves and photovoltaic parameters for control and D35-sensitized PSCs after 30 and 60 min of annealing are presented in Figure 5 and Table 1. It is obvious that the control devices showed a clear decline in their performance attributed to thermal treatment, ending in a 67% loss of their initial PCE, mainly associated with decrease in the J_{sc} value. On the other hand, the reference devices lose 30% of their initial PCE presenting an enhanced performance after thermal stress tests.

Table 1. Photovoltaic parameters of the as prepared cells under 1 sun illumination prepared with and without D35 after 5, 30 and 60 minutes of annealing at 100°C.

V_{oc} : open-circuit voltage, J_{sc} : short-circuit current density, FF: fill factor, PCE: power conversion efficiency

Device	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
TiO ₂ (5 min)	0.89	20.10	0.69	12.50
TiO ₂ (30 min)	0.82	17.34	0.65	6.50
TiO ₂ (60 min)	0.79	8.22	0.60	4.10
TiO ₂ /D35 (5 min)	0.88	24.00	0.68	14.00
TiO ₂ /D35 (30 min)	0.88	23.30	0.67	13.60
TiO ₂ /D35 (60 min)	0.87	18.83	0.62	10.80

CONCLUSIONS

In summary, we presented a totally novel strategy of titania compact layer/perovskite interface modification via adsorption of the D35 sensitizer in order to enhance the stability of perovskite solar cells. As a result, more stable devices were obtained due to the role of D35 which acts as a versatile shield layer over titania, improving the interface between the perovskite and the titania compact layer. This study paves the way for interface engineering aspiring to contribute in stability enhancement of perovskite solar cells towards further development including large-scale practical applications.

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