

High Efficiency Perovskite Solar Cells Fabricated under Ambient Conditions with Mesoporous $\text{TiO}_2/\text{In}_2\text{O}_3$ Scaffold

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Abstract—Mesoscopic perovskite solar cells (mp-PSCs) with mesoporous bilayer were fabricated under ambient conditions. The bilayer was formed by capping the mesoporous TiO_2 layer with a layer of In_2O_3 . $\text{CH}_3\text{NH}_3\text{I}_{3-x}\text{Cl}_x$ mixed halide perovskite was prepared through the one-step method and was used as the light absorber. The mp-PSCs with the composite $\text{TiO}_2/\text{In}_2\text{O}_3$ mesoporous layer exhibited optimized electrical parameters, compared with the PSCs that employed only a TiO_2 mesoporous layer, with a current density of 23.86 mA/cm^2 , open circuit voltage of 0.863 V , fill factor of 0.6 and a power conversion efficiency of 11.2% . These results indicate that the formation of a proper semiconductor capping layer over the basic TiO_2 mesoporous layer can facilitate the electron transfer, suppress the recombination and subsequently lead to higher charge collection efficiency.

Keywords—Ambient conditions, high efficiency solar cells, mesoscopic perovskite solar cells, $\text{TiO}_2/\text{In}_2\text{O}_3$ bilayer.

I. INTRODUCTION

IN the past years a new class of third generation photovoltaics has emerged based on organometal halide perovskites. While results of the first efficient perovskite solar cells (PSCs) were published in 2012 [1], their efficiencies were rapidly lifted to 20% the very next year. Moreover, in early 2016 researchers managed to manufacture PSCs with improved stability and a power output of 21.1% [2]. Perovskite materials are direct bandgap semiconductors described by the general formula ABX_3 , where X is an anion and A and B represent cations. The cation A is organic, typically methylammonium or formamidinium while cation B is lead (Pb) or tin (Sn) and the anion X is a halogen ion usually iodine, chlorine, bromine or a mixture of them [3]-[5].

For the fabrication of PSCs there are basically two different device architectures [6]. Planar or thin-film PSCs (Fig. 1 (a)) consist of a flat perovskite layer between n-type and p-type semiconductor. In this device structure, once the incident light is absorbed, the charge generation and the charge extraction are both occurring in the perovskite layer [7]-[9]. In the

mesoscopic or sensitized PSCs (Fig. 1 (b)) the active layer consists of a mesoporous semiconductor which is sensitized with the perovskite. The perovskite absorber infiltrates the semiconductor's layers creating a semiconductor-perovskite interface. Once the light is absorbed from the perovskite, the generated electrons are injected to the n-type semiconductor from where they are extracted and the holes are transferred to the p-type semiconductor [10], [11].

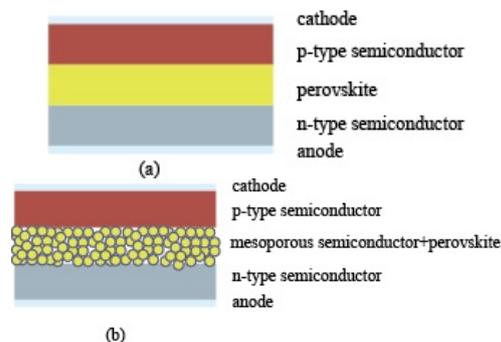


Fig. 1 Schematic figure of (a) planar (thin-film) and (b) mesoscopic (sensitized) PSCs [12]

In this work, we demonstrate the results of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ mixed halide organic-inorganic mesoscopic PSCs where the mesoporous layer is a combination of semiconductors, particularly TiO_2 and In_2O_3 . The combination of two (or more) different semiconductors can facilitate the electron transfer from the second semiconductor (In_2O_3) to the first one (TiO_2), provided that the conduction band edge of the second semiconductor is higher than the conduction band edge of the first semiconductor (Fig. 2) [13], [14]. Composite semiconductors have also been used in dye-sensitized solar cell (DSSC), which is another type of third generation photovoltaics, as they suppress the recombination processes and accelerate the electron transport, leading to higher charge collection efficiency [15], [16]. The structure that was used for the reference PSCs, without the additional step of the surface treatment of the mesoporous TiO_2 layer, was FTO/compact- TiO_2 /mesoporous- TiO_2 / $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ /P3HT/Au. For the PSCs with the capping layer of In_2O_3 the structure that was employed was FTO/compact- TiO_2 /mesoporous- $\text{TiO}_2/\text{In}_2\text{O}_3/\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ /P3HT/Au. These cells are compared against each other morphologically and electrically and the results are presented and discussed in the following paragraphs.

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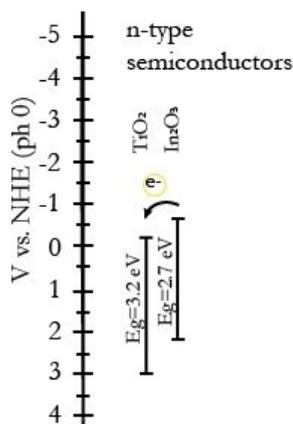


Fig. 2 Band gaps and band positions of the n-type semiconductors used for the mesoporous bilayer

II. EXPERIMENTAL

A. Materials

Titanium diisopropoxide bis(acetylacetonate) (75wt% in isopropanol, Aldrich), Titanium(IV) butoxide (97%, Aldrich), acetic acid, Pluronic P123 (5.800 MW, Aldrich), Indium(III) acetylacetonate (Aldrich), Triton X-100 (646.86 MW, Fisher Scientific), Hexamethylenetetramine (HMT), Hydroiodic acid, Anhydrous dimethylformamide (DMF), Pb(II) chloride (Acros organics), Chlorobenzene, Regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT, 95.5%, 94.000 MW, Ossila), Lithium Bis(trifluoromethane)sulfonimide (Li-TFSI, 99.95%, Aldrich), 4-tert butylpyridine (4-TBP, 96% Aldrich) and all solvents were used as received. Gold wire was sublimated to form the cathode.

B. PSCs Fabrication

All the fabrication processes were performed under ambient conditions. For fabricating the PSCs, fluorine-doped tin oxide (FTO) conductive substrates with a sheet resistance of 8 Ohm/square (Pilkington) were used, where a part of the conductive substrate was patterned by chemical etching with zinc powder and HCl aqueous solution. After the etching the conductive glasses were thoroughly cleaned with detergent solution and acetone in an ultrasonic bath and dried under nitrogen stream. A TiO₂ thin compact layer (c-TiO₂) was deposited on the FTO substrates by spin coating (2000 rpm, 10 s) using a titanium diisopropoxide bis(acetylacetonate) solution in isopropanol at a volumetric ratio of 1:9. The films were heated up to 500 °C for 10 min. Then six layers of porous TiO₂ solution were deposited by spin coating at 1200 rpm for 20 s. After each layer the films were calcined at 500 °C for 10 min. For the porous TiO₂ solution, 0.23 M Titanium(IV) butoxide, 0.4 ml acetic acid and 0.5 g Pluronic P123 were diluted in 4 ml isopropanol. Afterwards, a layer of In₂O₃ precursor solution was deposited on the prepared mesoporous TiO₂ films by spin coating at 3000, 4000 and 5000 rpm for 10 s, altering the layer's thickness. The solution was prepared by mixing 21 mg In(acac)₃, 7 mg HMT and 0.1 g Triton X-100 in 1 ml ethanol. For comparison, we prepared films with and without the In₂O₃

layer.

For methylammonium iodide (CH₃NH₃I) synthesis, 12 ml methylamine (33% in ethanol) and 5 ml HI (57% in water, Aldrich) were added in 20 ml ethanol in a 50 ml round-bottomed flask at 0 °C and reacted after 2 h. The solution was placed in a rotary evaporator to remove the excessive water and ethanol, resulting in a yellowish crystallized methylammonium iodide powder. Recrystallization of CH₃NH₃I was obtained after several washes with anhydrous diethyl ether until white powder was formed. Then, a 40 wt% precursor perovskite solution was formed by diluting methylammonium iodide and Pb(II) chloride in anhydrous DMF in a molar ratio 3:1. The porous TiO₂ films were deposited with perovskite solution by spin coating at 2000 rpm for 45 s. The prepared films were dried on a hot plate at 100 °C for 30 min under ambient conditions. Poly-3-hexylthiophene (94.000 g/mol) was diluted in chlorobenzene (15 mg/ml), dissolving 25 mM Lithium bis(trifluoromethanesulfonyl) imide and 76 mM 4-TBP as additives in order to improve the electrical characteristics. Two layers of P3HT were deposited on the films by spin coating at 1200 rpm for 10 s. After each layer the films were dried on a hot plate at 60 °C for 5 min in order to evaporate chlorobenzene [16]. Finally, all the samples were placed inside a high vacuum chamber (10⁻⁶ Torr) to sublimate non-corrosive gold to form the back contacts.

C. Characterization

The films' morphology, before applying the perovskite film, was examined using a Field Emission Scanning Electron Microscopy (FE-SEM, FEI Inspect™ F50) to determine whether the additional In₂O₃ layer alters the surface's structure. Current density-voltage (J-V) curves were obtained using a solar simulator Solar Light (16S-300) equipped with a Xenon lamp (measured at 100 mW/cm² with a Newport power meter, Model 843-R) and a Keithley 2601A source meter. The time delay between the data points in the J-V characteristic curves was set to 50 ms to ensure that no open-circuit voltage drop would occur [17].

III. RESULTS AND DISCUSSION

The top view images from the FE-SEM microscopy presented in Fig. 3 show no discrete morphology differences. Particularly, no apparent alterations were observed to the nanoparticles' size or the film's formation upon the deposition of the additional layer of In₂O₃. The films are highly porous, exhibiting large agglomerated clusters which can facilitate the perovskite solution infiltration.

Indium oxide was successfully combined with titanium dioxide and used as photoanode in PSCs. The current density – voltage (J-V) characteristic curves are presented in Fig. 4. It is obvious that the PSCs with the combined oxides TiO₂-In₂O₃ exhibit higher efficiencies than the cells with pure TiO₂ photoanode. Specifically, the highest efficiency (11.20%) is exhibited for the case of TiO₂-In₂O₃ photoanode where the In₂O₃ layer was deposited by spin coating in 3000 rpm, which corresponds to a 23% increase of the efficiency compared with

pure TiO_2 photoanode. Generally, In_2O_3 layer acts as a barrier layer that suppresses the electron – hole pair recombination rate resulting mainly in an increase of the current density, whereas the voltage remains nearly constant. Thus the overall performance is improved. The measured and calculated values of the short circuit current density (J_{SC}), open-circuit voltage (V_{OC}), maximum power (P_{MAX}), fill factor (FF) and power conversion efficiency ($\eta\%$) for all samples are summarized in Table I.

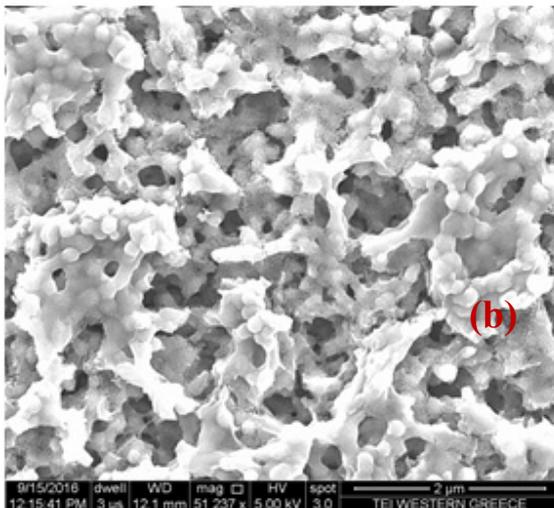
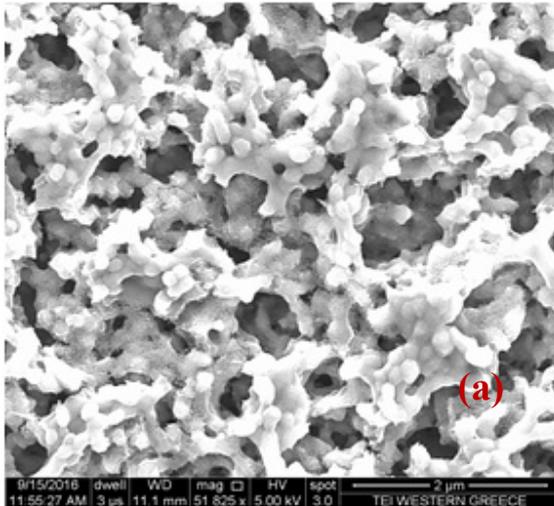


Fig. 3 FE-SEM images (a) of mesoporous TiO_2 film and (b) of mesoporous TiO_2 and In_2O_3 bilayer

IV. CONCLUSION

This work presents the fabrication and characterization of hybrid organic-inorganic mixed halide PSCs under ambient condition. mp-PSCs with plain TiO_2 mesoporous layer are compared against cells having a capping In_2O_3 layer over the mp- TiO_2 layer. Optimized electrical parameters were measured for the solar cells with the composite $\text{TiO}_2\text{-In}_2\text{O}_3$ mesoporous layer, which was ascribed to the fact that the top

In_2O_3 layer facilitates the electron transfer and suppresses the recombination rate leading to higher power conversion efficiencies. The highest efficiency that was achieved was 11.2% which is a satisfactory performance for mp-PSCs with a simple structure fabricated without having controlled conditions or using expensive equipment, such as glove box.

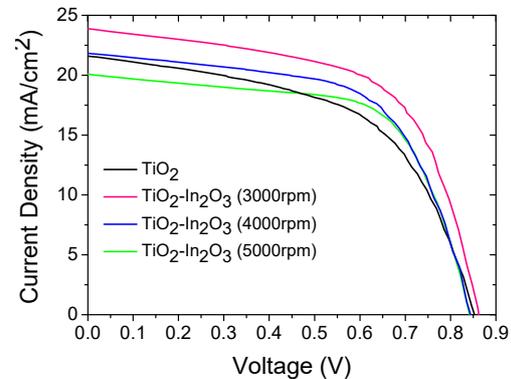


Fig. 4 Electrical characteristics of the PSCs with TiO_2 and $\text{TiO}_2\text{-In}_2\text{O}_3$ photoanodes, with different deposition speeds of the In_2O_3 layer

TABLE I
ELECTRICAL CHARACTERISTICS OF PSCS

Cell	J_{SC} (mA/cm^2)	V_{OC} (V)	P_{MAX} (mW)	FF	η (%)
TiO_2	21.59	0.853	0.794	0.55	9.13
$\text{TiO}_2\text{-In}_2\text{O}_3$ (3000rpm)	23.86	0.863	0.887	0.60	11.20
$\text{TiO}_2\text{-In}_2\text{O}_3$ (4000rpm)	21.85	0.843	0.876	0.61	10.21
$\text{TiO}_2\text{-In}_2\text{O}_3$ (5000rpm)	19.97	0.841	0.596	0.65	9.85

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