Fabrication of Stable and Efficient 2D/3D Perovskite Solar Cells through Post-treatment with $TBABF_4$

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Keywords

Thermal stability, 2D-3D perovskite, Perovskite solar cells, Mixed-dimensional

Experimental details

Synthesis of materials

All the organic methylammonium halides (MAI, MACl, and MABr) and formamidinium iodide (FAI) were prepared as reported by Li *et al.* [1]. Lead iodide (PbI_2) was also synthesized. For this purpose, 25 g of potassium iodide (KI, 99.5%, Merck) and 25 g of lead(II) nitrate ($Pb(NO_3)_2$, 99.5%, Merck) were dissolved in 1 L of distilled water under stirring on hotplates till the temperature of both solutions reached 80°C followed by more stirring for an hour. After that, the $Pb(NO_3)_2$ solution and 0.5 ml of an HCl solution (2 M) were added to the KI solution. The final solution was stirred for 30 min, cooled down and left at rest for 24 h, The obtained precipitates were filtered and washed with distilled water for four times. Finally, the gold color crystals were dried at 85°C in an oven for 8 h.

Solution preparation

$CsPbI_3$, PbI_2, and FAI/MABr/MACl precursor solutions were prepared as reported by Wang *et al.* [2]. A $CsPbI_3/PbI_2$ solution was also prepared by the addition of the $CsPbI_3$ precursor to the PbI_2 solution (1:10 v/v). Finally, a precursor solution of HTL (spiro-OMeTAD) was prepared as reported by Ahmed *et al.* [3].

Device fabrication

A pre-patterned F-doped SnO_2 (FTO, 15 Ω/sq, Solaronix) substrate was cleaned with an ultrasonic bath cleaner using soap, deionized water, acetone and isopropyl alcohol consecutively for 10 min. A thin compact TiO_2 (c-TiO_2) film was coated on the FTO substrate at 4000 rpm for 60 s using a solution of titanium(IV) tetraisopropoxide (TTIP, 98%, EXIR) in mixed solvents of ethanol (99%, Merck) and dimethylamine (99%, Merck). This was followed by baking at 500°C for an hour. A mesoporous TiO_2 (mp-TiO_2) layer modified with reduced graphene oxide (RGO) was spin-coated on the FTO/c-TiO_2 substrate at 4000 rpm for 60 s, followed by baking at 500 °C for an hour. To prepare a modified mp-TiO_2 solution, the TiO_2 paste (Sunlab, 20 nm paste) was diluted in ethanol (1:5 wt%), and then 4% (v/v) of reduced graphene oxide (99%, Sigma-Aldrich) dispersed in dichlorobenzene (DCB, 99%, Merck) (1 mg/ml) was added to the diluted mp-TiO_2 precursor, followed by stirring for 30 min. The perovskite films were fabricated through

a two-step deposition method under argon ambient [4]. For the post-treatment of the perovskite film with tetrabutylammonium tetrafluoroborate ($TBABF_4$, 99%, Sigma-Aldrich), a solution of $TBABF_4$ in chloroform (CF) with different concentrations was spin-coated on a cooled perovskite layer at 5000 rpm for 20 s, followed by annealing at different temperatures for 5 min. After that, a hole transfer layer (HTL) was spin-coated at 5000 rpm for 30 s on top of the perovskite layer using a spiro-OMeTAD solution. Finally, a 100-nm Au electrode layer was sputtered on the HTL.

Characterization

The surface quality of the perovskite layers was studied with SEM (TESCAN, Vega 3) images. The x-ray diffraction patterns of the perovskite films were collected with a Bruker, D8 advance x-ray diffraction spectrometer. The UV-vis spectra of the perovskites were obtained using an Ocean Optics, USB4000 UV-VIS spectrophotometer. Photoluminescence (PL) spectra were also plotted using an Agilent, Varian Cary Eclipse Fluorescence spectrometer system. The photovoltaic characteristics of the perovskite solar cells were recorded using a digital Keithley Model 2400 under the simulated irradiation of 100 mW/cm^2.

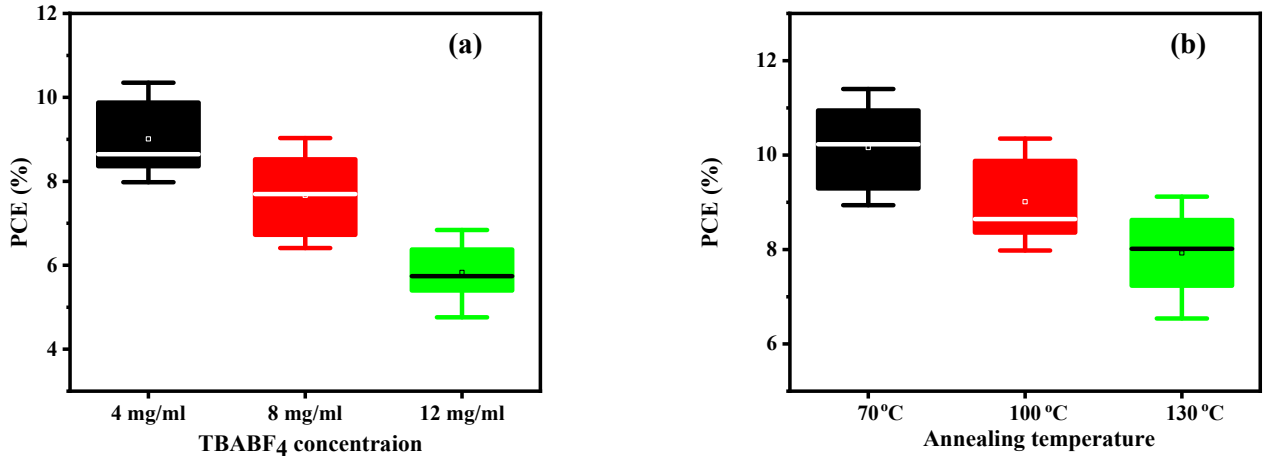

Figure S1. (a) The statistical PCE distribution of the fabricated HTL-free perovskite solar cells (PSCs) with different concentrations of the $TBABF_4$ solution at the post-treatment step. The annealing temperature for all the concentrations was 100°C. (b) The statistical PCE distribution of the fabricated HTL-free PSCs at different annealing temperatures for the perovskite layer treated with a 4 mg/ml of $TBABF_4$ solution

Table S1. Photovoltaic parameters of HTL-free perovskite solar cells with different concentrations of $TBABF_4$ and post-annealing temperatures

Device		Voc[a] (V)	J_{sc}[b] (mA/cm^2)	FF[c] (%)	PCE[d] (%)
4 mg/ml & 100 °C	Average	0.83	18.77	57.19	9.01
	Best	0.86	19.92	60.52	10.35
8 mg/ml & 100 °C	Average	0.81	17.68	55.73	7.67
	Best	0.83	19.13	56.67	9.03
12 mg/ml & 100 °C	Average	0.78	14.45	53.21	5.83

4 mg/ml & 70 °C	Best	0.81	15.33	55.16	6.84
	Average	0.86	19.10	58.45	10.16
4 mg/ml & 130 °C	Best	0.89	20.75	62.12	11.40
	Average	0.81	18.07	56.04	7.93
	Best	0.83	19.20	57.02	9.12

[a] Voc: open-circuit voltage; [b] Jsc: short-circuit current density; [c] FF: fill factor; [d] PCE: power conversion efficiency

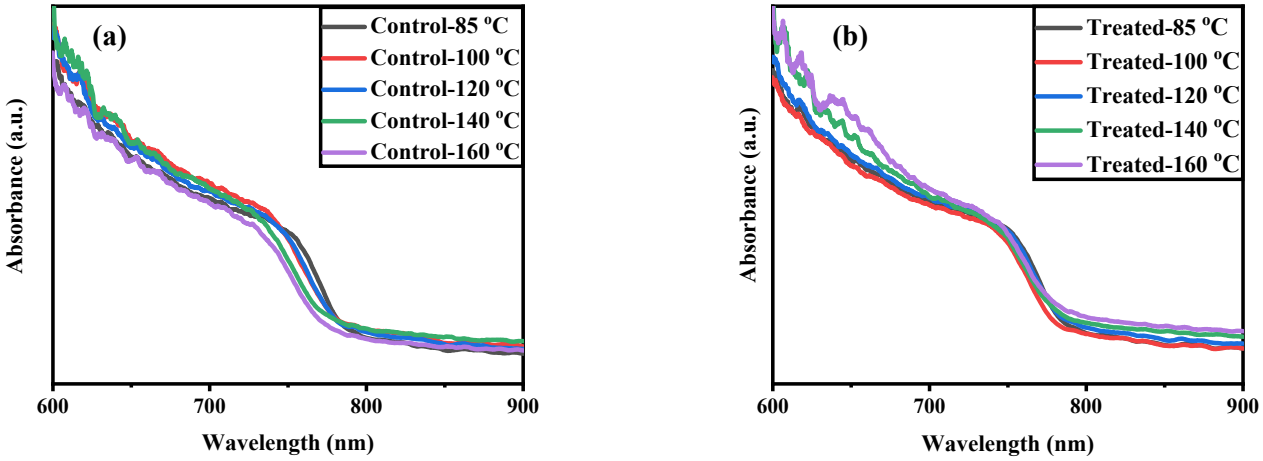

Figure S2. UV–vis absorption spectra for (a) the control perovskite film and (b) the film post-treated with $TBABF_4$ after annealing in the temperature range of 85-160°C with a holding period time of 30 min for each step. These measurements were conducted for the thermal stability of the perovskite films.

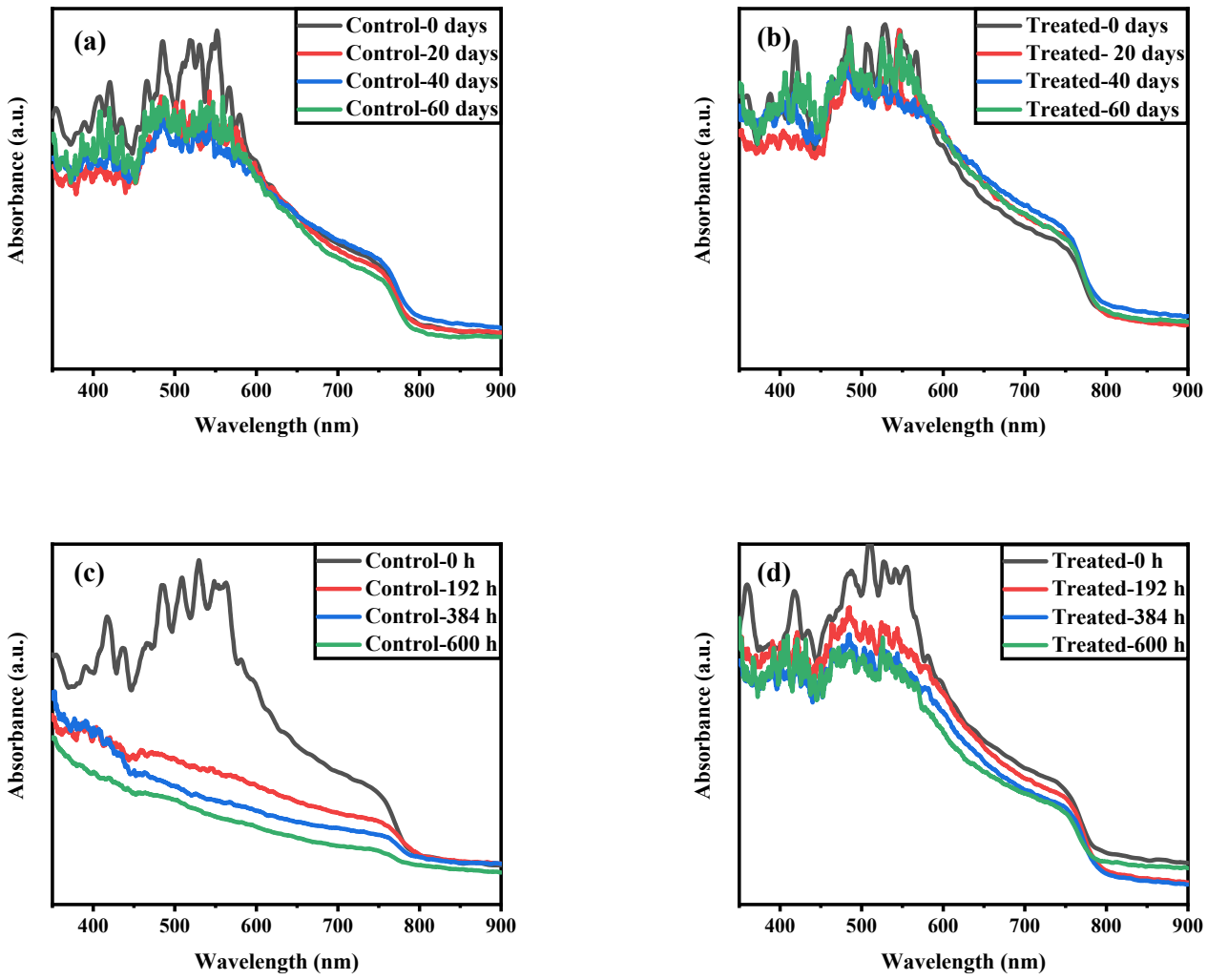

Figure S3. UV-vis absorbance spectra of (a, c) the control perovskite film and (b, d) the treated perovskite film for dry box and ambient air stability tests respectively

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