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# Journal of Materials Chemistry C

Materials for optical, magnetic and electronic devices

# Accepted Manuscript

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#### 1 Fabrication of Stable and Efficient 2D/3D Perovskite Solar Cells through Post-treatment with TBABF<sub>4</sub>

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#### 6 Abstract

7 Perovskite solar cells (PSCs), with their low cost and simple fabrication, have emerged as promising 8 devices to solve global warming issues. In this study, tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) was 9 used as a passivator to boost the performance and the stability of the fabricated PSCs. Through  $TBABF_4$ 10 post-treatment, the perovskite film's grain boundaries were passivated, which caused a reduction of charge traps on the surface of the perovskite layer and served as interfacial engineering at the perovskite/ 11 12 hole transport layer (HTL) interface. It was found that TBABF<sub>4</sub> can act as a source of TBA<sup>+</sup> cation and cause 13 to form a 2D/3D heterostructure layer, which increases the stability of PSCs. Indeed, 2D/3D structure 14 derived from TBABF<sub>4</sub> solution plays the role of a shield layer to protect the surface of perovskite layer from degradation and facilitates charge transport processes. The post-treatment of perovskite films is, 15 16 thus, introduced as an approach to address both the stability and the performance of PSCs and as a step 17 forward to commercialize PSCs.

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

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#### 1. Introduction

In recent years, perovskite solar cells (PSCs) have emerged as a promising application to meet the energy demands of the world <sup>1-3</sup>. The unique optoelectronic properties of perovskite materials <sup>4-6</sup> and their lowcost fabrication <sup>7</sup> have universally promoted them as appropriate candidates for producing solar cells. In the past decade, the goal of many researchers was the improvement of the photovoltaic (PV) performance of PSCs by suppressing charge recombination in perovskite layers or at the perovskite/charge interfaces of transport layers <sup>8-10</sup>, tailoring the composition of perovskite layers <sup>11, 12</sup>, passivating grain boundaries <sup>13-15</sup> and reducing the surface defects of perovskite films <sup>16, 17</sup>.

Perovskite materials are known with a general ABX<sub>3</sub> formula <sup>18, 19</sup>, wherein A is an organic cation (MA<sup>+</sup>(CH<sub>3</sub>NH<sub>2</sub><sup>+</sup>), FA<sup>+</sup>(CH(NH<sub>2</sub>)<sub>2</sub><sup>+</sup>) or an inorganic cation (Cs<sup>+</sup>, Rb<sup>+</sup>) at the hexahedral vertices, B is a metal cation (Pb<sup>2+</sup>, Sn<sup>2+</sup>, Ge<sup>2+</sup>) in the center, and X is a halide anion (Cl<sup>-</sup>, Br<sup>-</sup>, l<sup>-</sup>, or SCN<sup>-</sup>) which coordinates the B cations. Among perovskite materials, MAPbl<sub>3</sub> with a bandgap of ≈1.55 eV is the most extensively used material in PSCs <sup>20-22</sup>. The maximum PCE reported for MAPbl<sub>3</sub>-based PSCs is 21.2%, obtained through the modification of electron transporting layers (ETLs) <sup>23</sup>. FAPbl<sub>3</sub> is another perovskite material widely used as a light-harvesting layer in PSCs. Its desirability is due to the lower bandgap of about ≈1.43 eV <sup>24, 25</sup>. This material has two perovskite phases, known as  $\alpha$  and  $\delta$  phases <sup>26</sup>. The black  $\alpha$ -phase of FAPbI<sub>3</sub> perovskite is useful for PV application, while its yellow  $\delta$ -phase, known as the non-perovskite phase, is not favorable <sup>27, 28</sup>. The partial substitution of Cs<sup>+</sup>, Rb<sup>+</sup>, and MA<sup>+</sup> with FA<sup>+</sup> has been introduced as an effective approach to stabilize the photoactive  $\alpha$ -phase of FAPbI<sub>3</sub> perovskite <sup>26, 28-33</sup>. A PCE of 23.4% was reported for FAPbI<sub>3</sub>based PSCs. It was obtained by the incorporation of methylammonium chloride (MACl) into a FAPbI<sub>3</sub>

6 precursor solution <sup>28</sup>.

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7 Both pure MAPbl<sub>3</sub> and FAPbl<sub>3</sub> PSCs have achieved high PCE values, but they suffer from low intrinsic stability. The low stability disadvantage of PSCs should be addressed, and further efforts should be made 8 9 to industrialize PSCs. Different ISOS standards <sup>34</sup>, such as, dark storage (ISOS-D), thermal cycling (ISOS-T), 10 and light-soaking (ISOS-L) have been considered to study the stability issue of PSCs. Saliba et al. showed 11 that adding a small amount of Cs<sup>+</sup> to the FA/MA perovskite would significantly improve the thermal and operational stability of PSCs <sup>35</sup>. Afterwards, the A-site cation engineering of perovskite materials was 12 developed for PSCs stabilization <sup>36-38</sup>. Researchers showed that adding Rb<sup>+ 39</sup>, K<sup>+ 40</sup>, or Gu<sup>+ 41</sup> to triple-cation 13 Cs/FA/MA could further boost the PV performance and the stability of Cs/FA/MA PSCs. 14

Recently, the dimensional engineering of perovskite materials to form 2D/3D bi-layered structures on the 15 top of 3D perovskites has served as a most promising approach to improving the efficiency and stability 16 of PSCs <sup>6, 42</sup>. Hu et al., for the first time, combined 2D perovskite (PEA)<sub>2</sub>(MA)<sub>4</sub>Pb<sub>5</sub>I<sub>16</sub> with 3D perovskite 17 18 MAPbl<sub>3</sub> to form a 2D/3D heterostructure. They showed that the 2D/3D approach could boost the performance and stability of 3D PSCs <sup>43</sup>. Niu et al. compared different spacer ligands such as FBA, FPEA, 19 BA and PEA to fabricate 2D perovskite  $(L)_2(FA)_{n-1}Pb_nI_{3n+1}$  (L refer to spacer ligands). They used FAPbI<sub>3</sub> in 3D 20 21 perovskite solar cells and deposited different 2D perovskites on the top of it. They also showed that FPEAbased 2D/3D PSCs have higher stability than other spacers <sup>44</sup>. Yao et al. employed a 2D/3D bi-layered 22 23 structure to improve both the efficiency and the stability of triple-cation PSCs. They incorporated npropylammonium iodide (PAI) in a 3D perovskite layer <sup>45</sup>. 24

25 Considering the above discussion, this research aims at the fabrication of highly stable and efficient PSCs. 26 For this purpose, tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) is introduced as a source of TBA<sup>+</sup> 2D 27 cation for the post-treatment of a triple-cation Cs/FA/MA perovskite layer and the formation of a 2D/3D heterostructure layer. It has been found that TBABF<sub>4</sub> can passivate the grain boundaries of perovskite 28 29 layers and subsequently improve the PV performance of PSCs. The results show that, through TBABF<sub>4</sub> 30 post-treatment, surface defects and non-radiative charges recombination are decreased. Through the 31 post-treatment approach practiced in this study, a considerable PCE of 17.02% is achieved, which is higher 32 than that of 14.01% for control devices. Additionally, it has been observed that TBABF<sub>4</sub>-based PSCs are 33 more resistant to heat and humidity than control devices. Overall, the results prove that TBABF<sub>4</sub> post-34 treatment is a trustworthy approach for boosting the PCE and stability of PSCs through passivating the 35 grain boundaries and reducing the trap-state density of perovskite films.

#### 36 2. Results and discussion

In this study, the PV properties and the stability of triple-cation PSCs were improved through the post treatment of perovskite films with a TBABF<sub>4</sub> solution. To this end, first, the effects of TBABF<sub>4</sub> concentration

BF4

CH<sub>3</sub>

 $CH_3$ 

and the post-annealing temperature of the treated perovskite film on its properties were studied to 1

2 optimize the approach. Then, PSCs were fabricated via a two-step sequential deposition method (To find

3 more details, see the Experimental Section in Supporting Information). Figure 1 presents a schematic 4

diagram for the fabrication of PSCs without and with TBABF<sub>4</sub> post-treatment (i.e., control devices and

(b)

N

H<sub>3</sub>C

H<sub>3</sub>C

5 treated devices respectively).



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CsPbI3/PbI2 (a) 70°C CsPbI3/PbI2 FAI/MABr/MACl Annealing

Figure 1. (a) Schematic illustration of the fabrication process for the control perovskite solar cells (PSCs) (top) and the PSCs post-treated with tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) (bottom). (b) Chemical structure of the TBABF<sub>4</sub> salt

#### 7 2.1. Probing the effects of TBABF<sub>4</sub> on perovskite film properties

Annealing

FAI/MABr/MACl

for 15 min

150°C

TBABF<sub>4</sub>

5

Annealing

8 Figure 2a shows the UV-vis absorption spectra of the perovskite films treated with different 9 concentrations of the TBABF<sub>4</sub> solution. As it was observed, an increase in the concentration of the TBABF<sub>4</sub> 10 solution to 4 mg/ml would lead to a remarkable increase in the absorbance capacity of the corresponding 11 perovskite film within the visible range. Further increase in the TBABF<sub>4</sub> concentration, however, would 12 lead to the reduction of the absorbance of the perovskite film step by step. Figure 2b shows the UV-vis 13 absorbance spectra of the perovskite film treated with 4 mg/ml of TBABF<sub>4</sub> solution, followed by different 14 post-annealing temperatures. From these spectra, it can be found out that the post-annealing 15 temperature of the treated film affected the optical properties of the perovskite film. As the results 16 showed, the absorbance of the perovskite film was improved when the temperature of 70°C was selected 17 for the post-annealing process of the treated perovskite film. Also, from the absorbance spectra of the perovskite films with and without the post-treatment step, it is clear that TBABF<sub>4</sub> treatment did not 18 change the edge-absorption position of the perovskite film <sup>46, 47</sup>. In the literature, high absorbance by PSCs 19 20 is usually attributed to the enlarged grains size of the perovskite, but there were no enlarged grains 21 observed in the present study (Figure 3). The question is, thus, why did the absorbance of the treated 22 perovskite film increase? As deduced, the lower absorbance in the untreated perovskite film was due to the non-perovskite phase of FAPbl<sub>3</sub> ( $\delta$ -FAPbl<sub>3</sub>) <sup>48</sup>, which vanished after the post-treatment of the 23 perovskite (Figure 5a). 24



**Figure 2.** (a) UV–vis absorption spectra of the control perovskite film and those post-treated with different concentrations of tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>). (b) UV–vis absorption spectra of the perovskite films post-treated with 4 mg/ml of TBABF<sub>4</sub> at different annealing temperatures

For a more profound study of the role of concentration and post-annealing temperature in the  $TBABF_4$ 1 2 post-treatment approach, the surface morphology of different perovskite films was examined through 3 top-view SEM images (Figure 3). As it was found, at the annealing temperature of 100°C for treated 4 perovskite films by increasing the concentration of TBABF<sub>4</sub> solution, the micromorphology of the 5 corresponding perovskite film would change. In the case of the sample treated with concentration of 4 6 mg/ml, compared to other solution concentrations, a desirable film could be achieved for PV applications. 7 As another observation, when the post-annealing temperature of the treated perovskite film increased 8 from 70°C (Figure 3e) to 100°C (Figure 3b) and even to 130°C (Figure 3f), some wrinkles and pinholes 9 appeared on the film, which would serve as centers for charge accumulation and were not favorable for 10 PSCs. Figure 3e clearly shows that, upon the TBABF₄ post-treatment in optimized conditions, i.e., 4 mg/ml solution of TBABF<sub>4</sub> and a post-annealing temperature of 70°C for treated perovskite film, the grain 11 boundaries (GBs) of the perovskite film were passivated well. This phenomenon led to a decrease of the 12 13 trap density in the GBs, resulting in the decline of the monomolecular recombination and the 14 improvement of the PV performance (Figure 6). To support the results obtained from UV-vis and SEM 15 measurements, HTL-free PSCs were fabricated with the TBABF<sub>4</sub> post-treatment step. Then, the effects of 16 the TBABF<sub>4</sub> solution concentration and the post-annealing temperature of the treated perovskite films on 17 the PV properties were carefully probed (For more details, see Figure S1 and Table S1). The results shown 18 in Figure S1 are in full agreement with the findings of this study.

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**Figure 3.** Top-view SEM images of (a) the control and the tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) post-treated perovskite films with different concentrations of (b) 4 mg/ml, (c) 8 mg/ml and (d) 12 mg/ml. The post-annealing temperature of the treated perovskite films for (b), (c) and (d) was

100°C. (e) and (f) Top-view SEM images of the 4 mg/ml TBABF<sub>4</sub>-treated perovskite films at the postannealing temperatures of 70°C and 130°C respectively

- 1 To further study the effects of the TBABF<sub>4</sub> additive on the morphology of perovskite film, cross-sectional
- 2 SEM and AFM were employed (Figure 4). From cross-sectional SEM images was found that the thickness
- 3 of mixed mp-TiO<sub>2</sub>/perovskite layer in both control and treated devices is about 500 nm. Besides, the root
- 4 mean square (RMS) roughness of the perovskite film before and after treatment shows a reduction of
- 5 16.02 nm to 12.92 nm, indicating a better perovskite film with lower surface traps.

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**Figure 4.** (a, b) Cross-sectional SEM images of FTO/c-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/control and treated perovskite films. Scale bar of SEM images is 500 nm. (c, d) AFM images of control and the treated perovskite films on FTO/c-TiO<sub>2</sub>/mp-TiO<sub>2</sub> substrate.

6 From here onwards, the fabricated perovskite films with and without optimized post-treatment step were 7 labeled as 'treated' and 'control'. In Figure 5a, the XRD patterns of the control and the treated perovskite 8 films are compared. The XRD characterizations show that, with the addition of TBABF<sub>4</sub> post-treatment 9 step, the peak intensity of the perovskite layer in the orientation of (001), (111) and (002) clearly 10 increased, resulting in improved perovskite crystallinity due to the perovskite treatment. This consistent 11 with the top-view SEM images (Figure 3). As it can be seen in the XRD pattern of the control film, there are two PbI<sub>2</sub> peaks at 12.56° and 38.56° as well as a light non-perovskite peak for the  $\delta$ -FAPbI<sub>3</sub> at 11.71°, 12 none of which is desirable for PSCs. After the perovskite treatment with TBABF<sub>4</sub>, the PbI<sub>2</sub> peaks were 13

8

2

-20

suppressed, and the δ-FAPbI<sub>3</sub> peak completely vanished. Besides, in the XRD pattern of the treated perovskite film, a low-angle peak was observed at 7.28°, which might have belonged to the twodimensional perovskite TBA<sub>2</sub>PbI<sub>4</sub>(BF<sub>4</sub>)<sub>4-x</sub> structure <sup>49, 50</sup>. As it was also observed, all the X-ray diffraction peaks of the treated perovskite film shifted toward lower angles, considering a slight expansion in the unit cell of perovskite caused by the incorporation of larger TBA<sup>+</sup> cation into the 3D perovskite crystal structure <sup>45, 49, 51</sup>. For better insight, the (001) plane for the control and the treated films is presented in Figure 5b. It can be concluded that the TBABF<sub>4</sub> treatment caused the formation of a 2D/3D bi-layered structure on





**Figure 5.** (a) XRD pattern of the perovskite film with (treated) and without (control) TBABF<sub>4</sub> treatment.  $\blacklozenge$  denotes the Pbl<sub>2</sub> phase,  $\blacktriangle$  denotes the non-perovskite phase ( $\delta$ -FAPbl<sub>3</sub>),  $\blacklozenge$  denotes the TiO<sub>2</sub> phase,  $\clubsuit$  denotes the FTO phase, and  $\blacksquare$  denotes the two-dimensional TBA<sub>2</sub>Pbl<sub>4</sub> phase. (c) Steady-state photoluminescence (PL) spectra of the control and the post-treated

Wavelength (nm)

perovskite films deposited on an FTO substrate. Inset of (c) represents the PL spectra of different perovskite solar cells with ETL and HTL layers.

1 To further investigate the effect of TBABF<sub>4</sub> post-treatment on the optical properties and the charge recombination processes of perovskite films, steady-state photoluminescence (PL) measurements were 2 3 conducted at the excitation wavelength of 405 nm. First, the PL spectra of the control and the treated perovskite films were measured on the FTO substrate (Figure 5c). It was found that both perovskite films 4 had a PL peak around 800 nm corresponding to the bandgap of 1.55 eV. This was consistent with previous 5 reports for triple-cation perovskite solar cells <sup>52, 53</sup>. The PL intensity of the treated perovskite film was 6 higher than that of the control perovskite film, which suggests the reduction of non-radiative 7 8 recombination in the perovskite film due to the  $TBABF_4$  treatment. The suppressed non-radiative 9 recombination in the treated perovskite layer also suggests surface defects passivation and GBs 10 passivation after the TBABF<sub>4</sub> treatment (See Figure 3) <sup>46, 54</sup>.

Device		Voc <sup>a</sup> (V)	J <sub>sc</sub> <sup>b</sup> (mA/cm <sup>2</sup> )	FF <sup>c</sup> (%)	PCE <sup>d</sup> (%)
Control	Average	0.95	21.55	61.71	12.59
	Best	0.96	22.60	64.50	14.01
Treated	Average	0.98	23.64	68.39	14.71
Treated	Best	0.99	24.23	71.20	17.02

Table 1. Photovoltaic parameters of different perovskite solar cells.

<sup>a</sup> Voc: open-circuit voltage; <sup>b</sup> Jsc: short-circuit current density; <sup>c</sup> FF: fill factor; <sup>d</sup> PCE: power conversion efficiency

#### 11 **2.2. TBABF**<sub>4</sub> effects on photovoltaic properties

12 To provide better insight, hole-only PSCs were fabricated with the configuration of 13 FTO/PEDOT:PSS/Perovskite/Spiro-OMeTAD/Au and the dark current-voltage (I-V) response of the control 14 and the treated hole-only devices were measured to calculate their trap density ( $N_t$ ) (Figures 7c and 7d). 15 The  $N_t$  was determined as follows:

$$N_t = \frac{2V_{TFL}\varepsilon_r\varepsilon_0}{qL^2} \tag{1}$$

where *q* is the electric charge, *L* (400 nm) is the thickness of the perovskite layer,  $\varepsilon_r$  is the relative dielectric constant of perovskite ( $\varepsilon_r = 47$  for FAPbI<sub>3</sub>),  $\varepsilon_0$  is the vacuum permittivity, and  $V_{TFL}$  is the trap-filled limit voltage. As it can be seen in Figure 6, the V<sub>TFL</sub> value obtained for the control and the treated devices was 0.41 V and 0.3 V respectively. The calculated hole trap density was also  $2.83 \times 10^{14} cm^{-3}$  for the control and  $2.07 \times 10^{14} cm^{-3}$  for the treated device, which was consistent with the higher PL peak intensity observed in the treated perovskite film (Figure 5c). The inset of Figure 5c shows the PL spectra of the control and the treated complete PSCs. It clearly shows a higher PL peak quenching in the treated PSCs,

- which implies the reduction of the charge recombination at the perovskite/HTL interface. The formation 1 2 of 2D/3D bi-layered due to the TBABF<sub>4</sub> post-treatment approach facilitated the charge transfer process at 3 the perovskite/HTL interface <sup>55</sup>, and, as schematically shown in Figure 7a, it blocked the charge 4 recombination. This was consistent with the higher PL quenching observed in the treated devices (Inset 5 of Figure 5c). This phenomenon explains the higher current-density in the treated PSCs than in the control 6 PSCs (Figure 6a) <sup>56</sup>. To provide evidence for this statement, the dark I-V responses of the control and the 7 treated PSCs were measured (Figure 7b). The dark current-density of the treated device was significantly 8 lower than that of the control cells. This indicates that more photogenerated current would flow through 9 the PSC to reduce direct shunting. It also suggests the suppressed charge recombination and leakage
- 10 current in the treated PSCs <sup>57, 58</sup>.



**Figure 6.** (a) The current density–voltage (J-V) curves for the champion control and the treated perovskite solar cells (PSCs). (b) The statistical PCE distribution of all the control and the treated PSCs. (c) J-V characteristics in reverse and forward scans of a typical device for control and treated PSCs. (d) The IPCE spectra of different PSCs and the integrated current densities from the IPCE.

The current density-voltage (J-V) characteristics of the best-performing PSCs for the control and the 1 2 treated devices are shown in Figure 6a. The active area of all PSCs to record J-V curves was 8 mm<sup>2</sup>. The 3 statistical PCE distribution of all the fabricated PSCs is presented in Figure 6b, and all the other 4 corresponding PV parameters are summarized in Table 1. A champion PCE of 14.01% was achieved for the control PSCs, with the open-circuit voltage (Voc), the short-circuit current density (Jsc) and the fill factor 5 6 (FF) of 0.96 V, 22.60 mA/cm<sup>2</sup> and 64.5% respectively. After the post-treatment step, a PCE of 17.02% was 7 obtained with the V<sub>oc</sub>, J<sub>sc</sub> and FF of 0.99 V, 24.23 mA/cm<sup>2</sup> and 71.2% respectively. Besides, in Figure 6d 8 the IPCE test was employed to show the  $J_{sc}$  improvement. The obtained values of  $J_{sc}$  from IPCE spectra 9 were 22.06 mA/cm<sup>2</sup> and 23.40 mA/cm<sup>2</sup> for control and the treated PSCs respectively, consistent with the average J<sub>sc</sub> value calculated from J-V curves (See Table 1).". All the PV parameters of the treated devices 10 11 were higher than those of the control devices. As earlier explained, the higher Voc obtained in the treated 12 devices is due to the lower trap density in them and the reduced non-radiative recombination. Also, the 13 higher J<sub>sc</sub> and FF for the treated devices are attributed to the suppressed charge recombination, blocked direct shunting, and suppressed non-perovskite  $\delta$ -FAPbI<sub>3</sub> phase caused by the formation of a 2D/3D bi-14 layered structure in the TBABF<sub>4</sub> post-treatment step. In addition, the hysteresis phenomenon (HI 15 16 (%)=((PCE<sub>reverse</sub>-PCE<sub>forward</sub>)/PCE<sub>reverse</sub>) × 100%) of PSCs was studied as shown in Figure 6c. It was found that

in treated PSCs the hysteresis index (HI) value reduces to 5.5% from 12% of that of the control device. The
lower HI in treated PSCs may be due to the GBs passivation of perovskite layer (Figure 3) and also
smoother perovskite layer (Figures 4c and 4d), which reduces the non-radiative recombination, and
facilitates charge transport processes at the perovskite/HTLs interface.





**Figure 7.** (a) Band diagram of the perovskite solar cells (PSCs) with and without  $TBABF_4$  post-treatment. Bands energy value as reported in <sup>59, 60</sup>. (b) The dark current density–voltage (J-V) for the control and the treated PSCs. Dark current–voltage characteristics of the hole-only device (FTO/PEDOT:PSS/Perovskite/Spiro-OMeTAD/Au) for (c) the control perovskite film and (d) the treated perovskite film

# 1 **2.3. Stability of the photovoltaic devices**

As an important parameter, the stability of the PSCs was studied against humidity and heat. At first, the 2 3 thermal stability (thermal cycling) of the control and the treated perovskite layers were monitored. For 4 this purpose, the perovskite films were exposed to different temperatures of 85°C, 100°C, 120°C, 140°C 5 and 160°C. The perovskite films were held at each temperature for 30 minutes, and the UV-vis absorption 6 spectra were measured. Then, the temperature was immediately increased for the next step. This process 7 was repeated up to the temperature of 160°C (See Figure S2). There was a change observed in the edge-8 absorption (EDA) position of the control perovskite film when the temperature of the thermal stability 9 test rose from 85°C to 160°C, suggesting a composition change in the control perovskite film. By contrast, 10 no change was observed in the EDA position of the treated perovskite film. So, it can be deduced that the 11 thermal stability of treated PSCs is higher than that of untreated PSCs.

12 To investigate the long-term humidity stability (ISOS-D protocols) of the control and the treated PSCs, four 13 devices in each group were kept in a dry box with a humidity of < 20% (Figure 8e) and ambient air with a 14 relative humidity of 20-45% (Figure 8d). Figure 8a shows the digital photographs of the control (top) and the treated (bottom) perovskite films during the stability test in ambient air. For both dry box and ambient 15 16 air stability tests, the UV-vis absorbance spectra of the corresponding perovskite films were periodically 17 measured (Figure S3). After 1440 hours of storage inside the dry box, the treated PV devices retained 18 about 90% of their initial efficiency, whereas a PCE loss of almost 30% occurred in the control devices. 19 Also, in the case of the ambient air test, after 600 hours, the treated PSCs had better ambient air stability 20 with a PCE loss of about 25%, as compared to the control PSCs which were degraded entirely during the 21 ambient air test. The same trend was observed in the UV-vis absorbance spectra of the devices during the 22 humidity tests (Figure S3). The observed results in ambient air stability are supported by the static contact-

angle measurements presented in Figures 8b and 8c. As can be seen, the water droplet contact angle on 1 2 the TBABF4 treated perovskite film is larger than that that of the control film, indicating reduced 3 hygroscopicity and improved water resistance in treated films. The enhanced hydrophobicity behavior of 4 the treated films is an important factor contributing to the improved stability of TBABF<sub>4</sub>-based PSCs. The stability tests results bring one to the conviction that the stability improvement of treated PSCs is due to 5 6 the formation of 2D/3D bi-layered and GBs passivation, caused by the TBABF<sub>4</sub> post-treatment approach. 7 As reported by Castro-Méndez et al. 61, the GBs in a perovskite layer are responsible for the unstable 8 behavior of PSCs. A perovskite film in humidity undergoes a degradation process beginning from the 9 surface, and the speed of degradation increases through GBs. GBs passivation is, thus, introduced as an 10 effective method to address the stability issue of PSCs.





**Figure 8.** (a) Digital photographs of the control and the treated perovskite films at 600 h in ambient air with a relative humidity of 20-45%. The contact-angle measurement of control (b), and treated perovskite film (c). (d) The stability test of the control and the treated perovskite solar cells at room temperature without encapsulation kept in ambient air with a relative humidity of 20-45% and (e) those stored in a dry box (< 20% RH) in a dark condition. Four devices of each type were utilized for the stability tests, and 5% of the error bars were adopted.

### 1 **3.** Conclusion

In this study, triple-cation PSCs were fabricated, and their performance and stability were improved by 2 using a TBABF<sub>4</sub> salt solution for the post-treatment of the perovskite layer. The TBABF<sub>4</sub> salt could serve as 3 a source for the TBA<sup>+</sup> cation to form a 2D/3D heterostructure layer on the top of a 3D perovskite layer. As 4 5 it was found, TBABF<sub>4</sub> treatment passivated GBs and reduced the trap density at the perovskite/HTL 6 interface, which improved the charge transport processes and reduced the charge recombination rate. 7 There was also a shift to a lower angle in the XRD pattern of the treated perovskite film, which proved the 8 formation of a 2D/3D structure. The results indicated that the presence of the 2D/3D layer on the top of 9 the 3D perovskite film and the passivation of GBs were both the result of the TBABF<sub>4</sub> post-treatment and 10 the increased the thermal and ambient air stability of PSCs. In brief, the TBABF<sub>4</sub> post-treatment approach provides a simple way to enhance the PV parameters and the stability of PSCs. 11

12

# 13 Acknowledgments

The authors wish to thank Iran National Science Foundation (INSF) for the financial support of this research (Research proposal No: 96003879).

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# Fabrication of Stable and Efficient 2D/3D Perovskite Solar Cells through Posttreatment with TBABF<sub>4</sub>

A promising 2D/3D heterostructure based on  $\mathsf{TBABF}_4$  salt to boost the performance and stability of perovskite solar cells

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