

Supporting Information

Spray-Pyrolyzed ZnO as Electron Selective Contact for Long Term Stable Planar $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Solar Cells.

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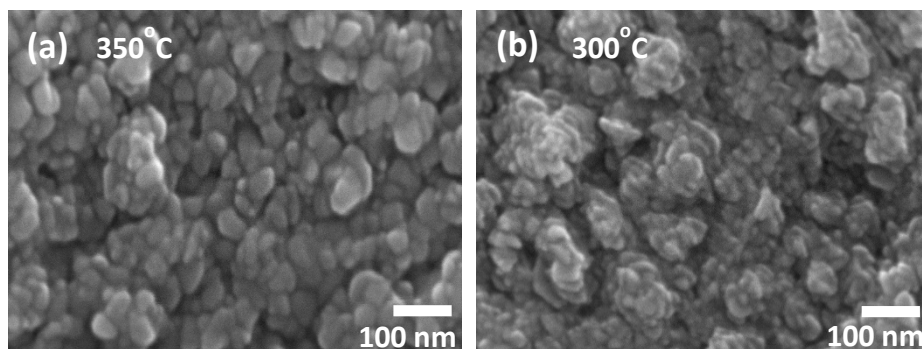
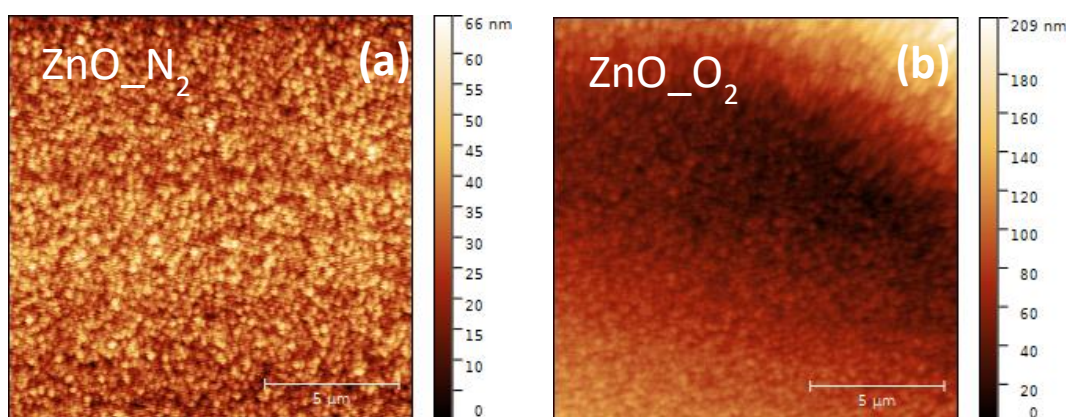


Figure S1. Top view SEM from secondary electrons of ZnO spray-pyrolyzed from 0.1 M zinc acetate solution at 350°C (a) and 300°C (b) with oxygen flow.



Supporting Information

Figure S2. Atomic force microscopy (AFM) of ZnO layer deposited on FTO from 0.3M of zinc acetate solution at 450°C with nitrogen (a, named ZnO_N₂) and oxygen flow (b, named ZnO_O₂).

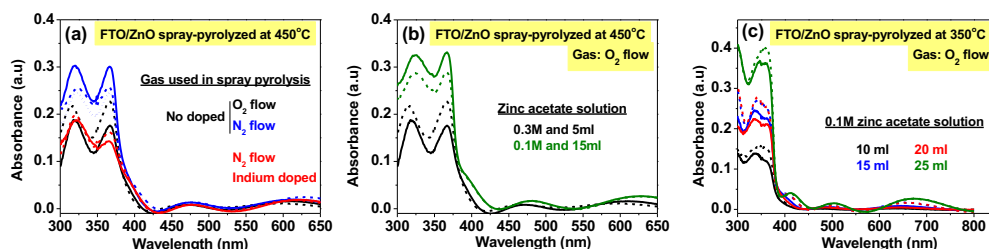


Figure S3. Absorbance spectra of spray-pyrolyzed ZnO from (a) 5 ml of 0.3 M zinc acetate solution at 450°C with nitrogen and oxygen flow; (b) different volume and zinc acetate concentration solution at 450°C with oxygen flow, the amount of Zn²⁺ ions was maintained the same in the spray solutions and (c) different volume of 0.1M zinc acetate solution at 350°C with oxygen flow.

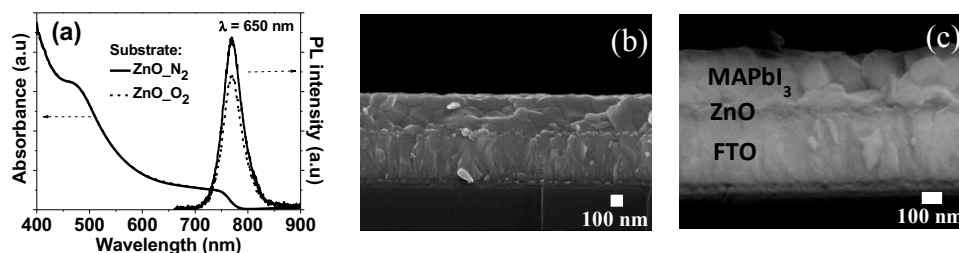


Figure S4. (a) Absorbance and photoluminescence (PL) of fresh MAPbI₃ on ZnO layer spray-pyrolyzed from 0.3 M zinc acetate solution at 450°C with nitrogen and oxygen flow. Cross section SEM images from secondary (b) and backscattered electrons (c) of fresh MAPbI₃ film deposited on ZnO prepared with N₂ flow.

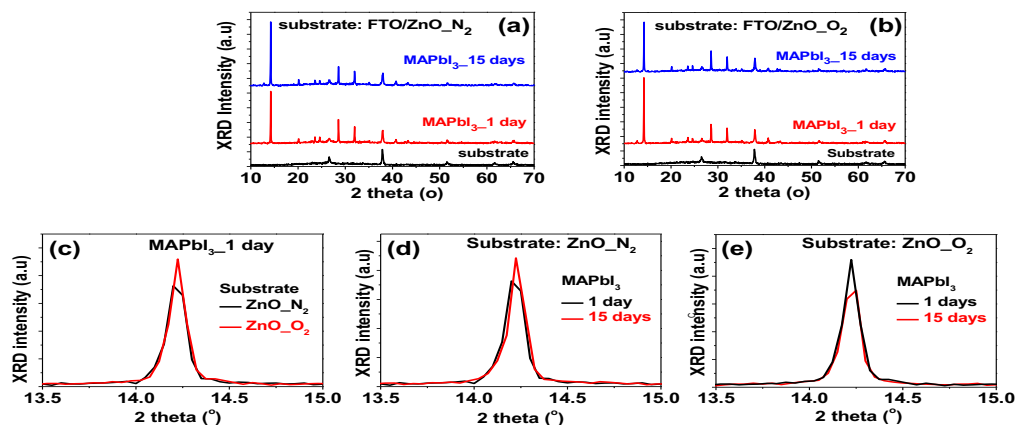


Figure S5. (a-b) XRD pattern of 1 day and 15 day-old MAPbI₃ deposited on FTO/ZnO_N₂ (a) and FTO/ZnO_O₂ substrates (b). In which ZnO was spray-pyrolyzed from 0.3 M zinc

Supporting Information

acetate solution at 450°C with nitrogen and oxygen flow. The XRD pattern of substrate is belong to SnO₂ (reference pattern: 9163). There is no detection of ZnO peaks due to its extremely thin thickness. (c-e) Comparison of XRD intensity at 14.2° of those MAPbI₃ films which were stored under dark and at room temperature and at around 35% of humidity.

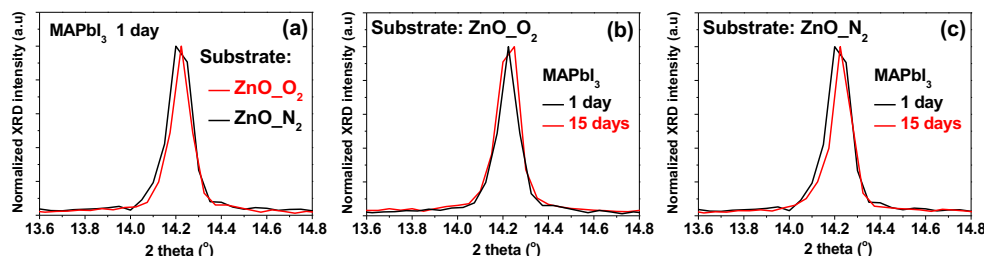


Figure S6. Normalized XRD intensity at 14.2° of (a) 1 day-old MAPbI₃ deposited on FTO/ZnO_N₂ and FTO/ZnO_O₂ substrates. And normalized XRD intensity at 14.2° of fresh (1 day) and old (15 days) MAPbI₃ film deposited on (b) FTO/ZnO_O₂ and (c) FTO/ZnO_N₂ substrates. In which ZnO was spray-pyrolyzed from 0.3 M zinc acetate solution at 450°C with nitrogen and oxygen flow. Those MAPbI₃ films which were stored under dark and at room temperature and at around 35% of humidity.

Table S1. Full width at half maximum (FWHM) and normalized XRD intensity of 1 day and 15 days-old MAPbI₃ film deposited on FTO/ZnO_N₂ and FTO/ZnO_O₂ compact layer. In which ZnO was spray-pyrolyzed from 0.3 M zinc acetate solution at 450°C with nitrogen and oxygen flow. MAPbI₃ films were stored under dark and around 35% of humidity.

| 2 theta (°) | FWHM | | | |
|----------------|-------------------------------|------------------------------|-------------------------------|------------------------------|
| | Substrate: ZnO_N ₂ | | Substrate: ZnO_O ₂ | |
| | MAPbI ₃ : 1 day | MAPbI ₃ : 15 days | MAPbI ₃ : 1 day | MAPbI ₃ : 15 days |
| 14.2 | 0.117 | 0.101 | 0.104 | 0.111 |
| 2 theta (°) | XRD intensity (%) | | | |
| | Substrate: ZnO_N ₂ | | Substrate: ZnO_O ₂ | |
| | MAPbI ₃ : 1 day | MAPbI ₃ : 15 days | MAPbI ₃ : 1 day | MAPbI ₃ : 15 days |
| 14.2 | 100 | 100 | 100 | 100 |
| 28.6 | 47.2 | 31.2 | 30.4 | 43.3 |
| 32 | 33.7 | 24.2 | 24.9 | 31.7 |

Supporting Information

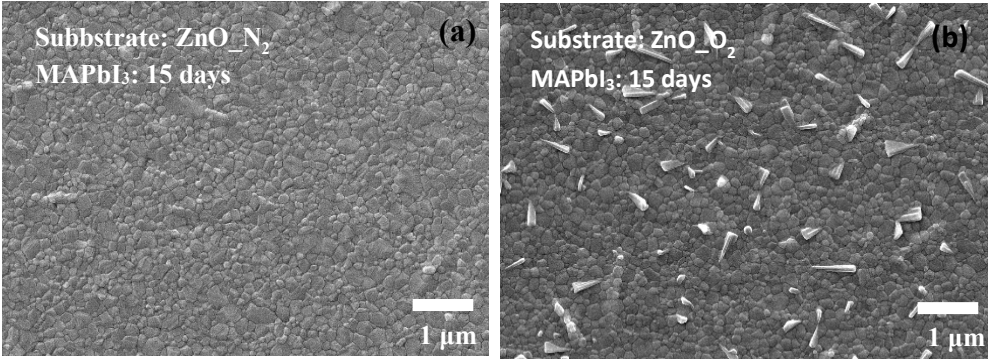


Figure S7. Low magnification top view SEM of 15 days-old MAPbI₃ deposited on FTO/ZnO_N₂ (a) and FTO/ZnO_O₂ substrates (b). In which ZnO was spray-pyrolyzed from of 0.3 M zinc acetate solution at 450°C with nitrogen and oxygen flow. MAPbI₃ films were stored under dark and at room temperature and at around 35% of humidity.

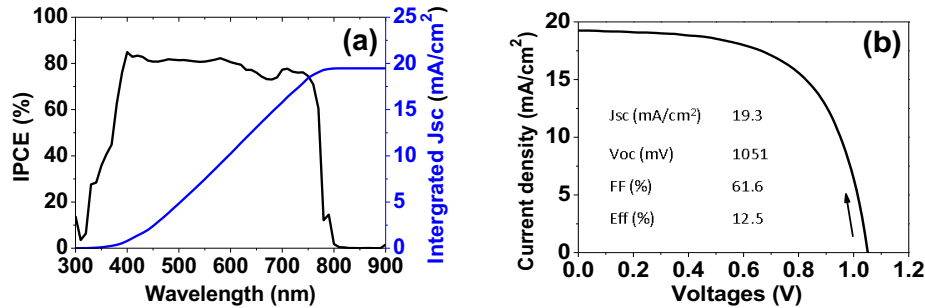


Figure S8. IPCE spectra and integrated short circuit current density (J_{sc}) of FTO/ZnO_N₂/MAPbI₃/Spiro OMeTAD/Au (a) and its J-V curve, reverse scan, measured at 1 sun illumination (b). In which ZnO was spray-pyrolyzed from 0.3 M zinc acetate solution at 450°C with nitrogen flow.

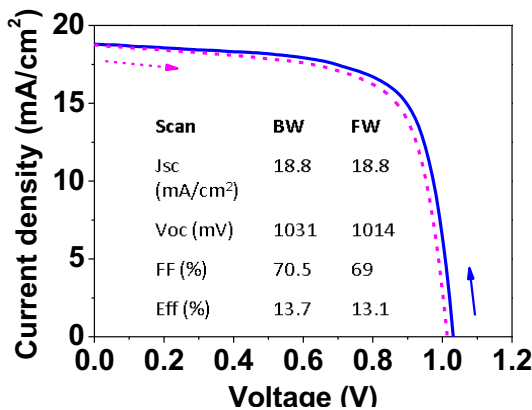


Figure S9. Current density-voltage (J-V) characteristic of best device after 34 days prepared with a structure of FTO/ZnO_N₂/MAPbI₃/Spiro OMeTAD/Au at 1 sun illumination. In which ZnO was spray-pyrolyzed from 0.3 M zinc acetate solution at 450°C with nitrogen flow. Sample was stored under dark at room temperature and at around 35% of humidity.

Supporting Information

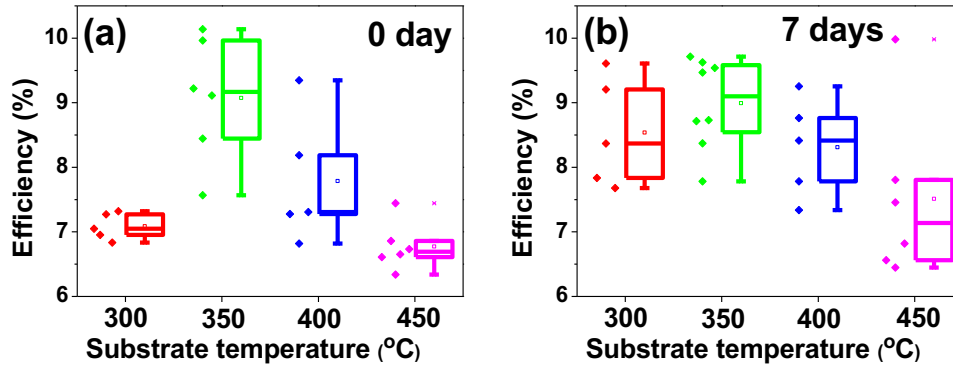


Figure S10. Performance at 1 sun illumination of planar based ZnO₂ devices with a structure of FTO/ZnO/MAPbI₃/Spiro OMeTAD/Au measured immediately (a) and 7 days after the preparation (b). In which ZnO was spray-pyrolyzed from 15 ml of 0.1 M zinc acetate solution at different substrate temperatures with oxygen flow. Full devices were stored under dark, at room temperature and at around 35% of humidity. The concentration of zinc acetate solution was reduced 1/3 times however the solution volume was increased 3 times to maintain the same amount of Zn²⁺, in comparison with the samples used in Table 1. The best efficiency for fresh devices was archived for ZnO prepared at 350°C and this value is similar to that obtained for ZnO spray-pyrolyzed at 450°C with higher concentration of zinc acetate solution (table 1 and table S2). The reason is at different solution concentrations and different substrate temperatures, ZnO was formed differently.

Table S2. Statistic photovoltaic parameters at 1 sun of planar based ZnO thin film devices showed in the Figure S10.

| Time [days] | Subs. temp [°C] | Jsc [mA/cm ²] | Voc [mV] | FF [%] | Eff [%] |
|-------------|-----------------|---------------------------|--------------|------------|-----------|
| 0 | 300 | 15.5 ± 0.1 | 934.2 ± 16.7 | 46.4 ± 0.7 | 7.1 ± 0.1 |
| 7 | | 16.1 ± 0.1 | 1006.2 ± 8.9 | 53.5 ± 1 | 8.5 ± 0.3 |
| 0 | 350 | 15.9 ± 0.1 | 1010.4 ± 9.4 | 50.2 ± 1.6 | 9.1 ± 0.3 |
| 7 | | 15.6 ± 0.2 | 1021.5 ± 6.9 | 57.8 ± 0.9 | 9 ± 0.2 |
| 0 | 400 | 16.9 ± 0.2 | 831.6 ± 21.8 | 52 ± 0.4 | 7.8 ± 0.4 |
| 7 | | 14.9 ± 0.1 | 981 ± 18.7 | 55.2 ± 0.5 | 8.3 ± 0.3 |
| 0 | 450 | 16.1 ± 0.2 | 773.4 ± 16.1 | 49.1 ± 1.2 | 6.8 ± 0.1 |
| 7 | | 13.8 ± 0.3 | 933.8 ± 17 | 57.9 ± 0.8 | 7.5 ± 0.4 |

Supporting Information

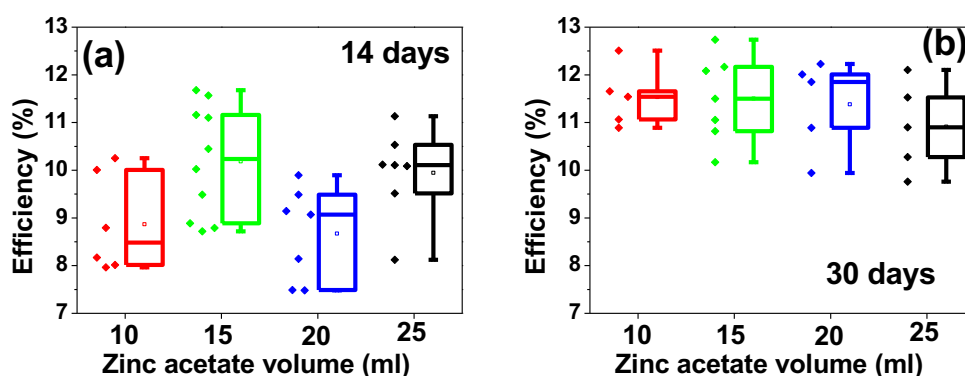


Figure S11. Performance at 1 sun illumination of planar based ZnO₂ devices with a structure of FTO/ZnO/MAPbI₃/Spiro OMeTAD/Au measured 14 days (a) and 30 days (b) after the preparation. In which ZnO was spray-pyrolyzed from different volume of 0.1 M zinc acetate solution at 350°C substrate temperatures with oxygen flow. Full devices were stored under dark and at room temperature and at around 35% of humidity.

Table S3. Statistic photovoltaic parameters of planar based ZnO thin film devices showed in the Figure S11.

| Time [days] | Zinc acetate volume [ml] | Efficiency [%] |
|-------------|--------------------------|----------------|
| 14 | 10 | 8.9 ± 0.3 |
| 30 | | 11.5 ± 0.3 |
| 14 | 15 | 10.1 ± 0.3 |
| 30 | | 11.3 ± 0.2 |
| 14 | 20 | 8.7 ± 0.3 |
| 30 | | 11.4 ± 0.4 |
| 14 | 25 | 9.9 ± 0.3 |
| 30 | | 10.9 ± 0.4 |

Table S4. Photovoltaic parameters at 1 sun illumination of fresh (0 day-old) planar based ZnO devices with a structure of ZnO/MAPbI₃/Spiro OMeTAD/Au. In which ZnO was spray-pyrolyzed from of 0.1 M zinc acetate solution at 300°C substrate (FTO or ITO) temperatures with oxygen flow.

| Substrates | Jsc mA/cm ² | Voc mV | FF % | Efficiency % |
|------------|------------------------|---------|-------|--------------|
| FTO/ZnO | 15.78 | 1067.35 | 45.14 | 7.60 |
| ITO/ZnO | 12.84 | 1012.12 | 59.70 | 7.76 |

Supporting Information

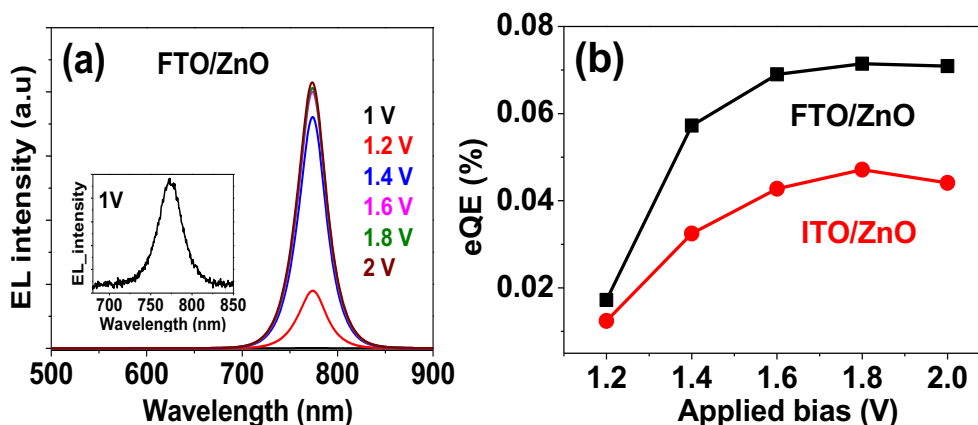


Figure S12. (a) EL spectra and eQE (b) of fresh (0 day-old) LED devices with a structure of ZnO/MAPbI₃/Spiro OMeTAD/Au at different applied bias. In which ZnO was spray-pyrolyzed from 0.1M zinc acetate solution at 300°C substrate (FTO or ITO) temperatures with oxygen flow.

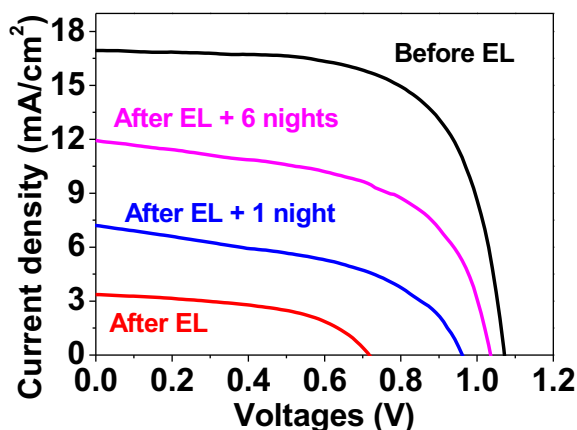


Figure S13. Performance at 1 sun illumination of un-encapsulated planar based ZnO devices with a structure of FTO/ZnO/MAPbI₃/Spiro OMeTAD/Au before and after the EL measurement at 1.8 V applied bias. In which ZnO was spray-pyrolyzed from 0.3M zinc acetate solution at 450°C with oxygen flow. Full devices were stored under dark and at room temperature and at around 35% of humidity. It is well known that after the electroluminescence (EL) measurement un-encapsulated MAPbI₃ devices degraded. Our devices showed a significant drop after the characterization as LED. However the performance was recovered partially with time storing the device under dark at room temperature and with a humidity of around 35%.

Supporting Information

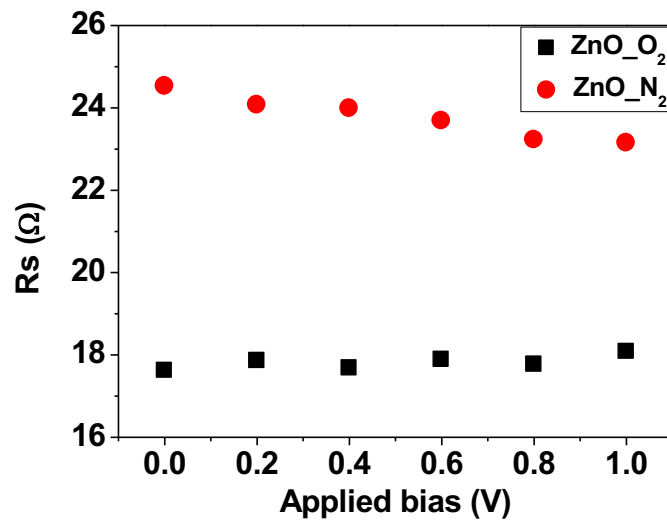


Figure S14. Fitted contact resistance, R_s , of impedance spectroscopy measurement of PSCs based on ZnO_N₂ or ZnO_O₂ substrates at 1 sun illumination

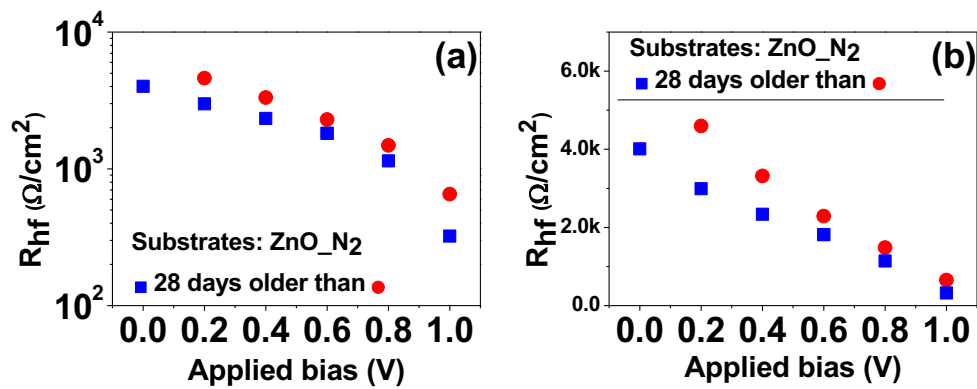


Figure S15. R_{hf} related to charge transport and to the recombination obtaining in the Figure 6, plotted in (a) log and (b) linear scale.