



Supplementary information

Low-Temperature Hydrothermal Growth of ZnO Nanowires on AZO Substrates for FACsPb(IBr)₃ Perovskite Solar Cells

Karthick Sekar^{1,2,3,*}, Rana Nakar¹, Johann Bouclé^{2,3}, Raphaël Doineau¹, Kevin Nadaud¹, Bruno Schmaltz⁴, and Guylaine Poulin-Vittrant^{1,*}

¹ GREMAN UMR 7347, Université de Tours, CNRS, INSA Centre Val de Loire, 37071 Tours, cedex 2, France; rana.nakar@univ-tours.fr (R.N.); raphael.doineau@univ-tours.fr (R.D.); kevin.nadaud@univ-tours.fr (K.N.)

² Univ. Limoges, XLIM, UMR 7252, 87000 Limoges, France.

³ CNRS, XLIM, UMR 7252, 87000 Limoges, France; johann.boucle@unilim.fr

⁴ PCM2E EA 6299, Université de Tours, Parc de Grandmont, 37200 Tours, France; bruno.schmaltz@univ-tours.fr

* Correspondence: karthick.sekar@univ-tours.fr (S.K.); guylaine.poulin-vittrant@univ-tours.fr (G.P.-V.)

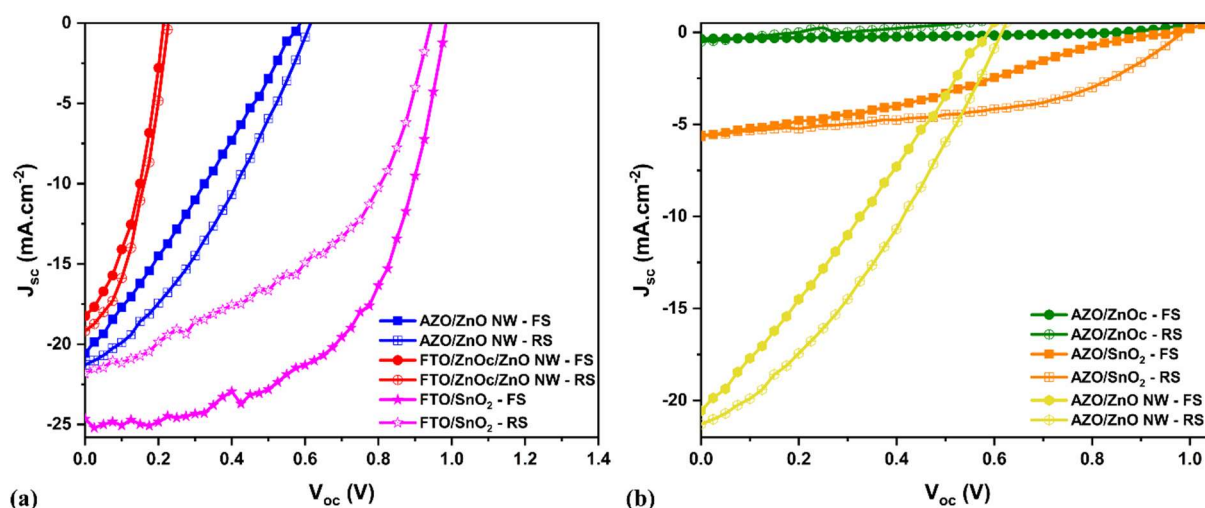


Figure S1. J–V characteristics of perovskite solar cells (best device) fabricated with different photoanodes of ZnO NWs depending on the seed layer. (a) comparison of AZO/ZnO NW, FTO/ZnO/ZnO NW, and FTO/SnO₂ devices, (b) Comparison of AZO/ZnO, AZO/SnO₂, and AZO/ZnO NW based devices, respectively.

Table S1. Performances of perovskite solar cells depending on the type of photoanodes.

| Device | Scan | | Jsc (mA.cm ⁻²) | Voc (V) | FF | PCE (%) | R _{sh} (Ω) | R _s (Ω) |
|--|------|---------|-------------------------------|------------|------|---------|------------------------|-----------------------|
| AZO/SnO ₂ /Perovskite/ Spiro-OMeTAD/Au | FS | Best | 5.6 | 0.95 | 0.31 | 1.7 | 1340 | 780 |
| | | Average | 5.3 | 0.95 | 0.25 | 1.3 | 1060 | 960 |
| | RS | Best | 5.6 | 0.98 | 0.49 | 2.7 | 2210 | 250 |
| | | Average | 5.3 | 0.98 | 0.47 | 2.4 | 2910 | 410 |
| AZO/ZnO/Perovskite/ Spiro-OMeTAD/Au | FS | Best | 0.3 | 0.49 | 0.45 | 0.1 | 21940 | 2840 |
| | | Average | 0.4 | 0.84 | 0.35 | 0.1 | 12990 | 3340 |
| | RS | Best | 0.3 | 0.27 | 0.43 | 0.1 | 13860 | 1670 |
| | | Average | 0.5 | 0.21 | 0.28 | 0.1 | 2440 | 2370 |
| AZO/ZnO NW/Perovskite/Spiro- OMeTAD/Au | FS | Best | 15.6 | 0.65 | 0.43 | 4.3 | 660 | 80 |
| | | Average | 16.4 | 0.66 | 0.36 | 3.8 | 430 | 110 |
| | RS | Best | 16.1 | 0.64 | 0.47 | 4.9 | 1400 | 70 |
| | | Average | 16.7 | 0.68 | 0.43 | 4.8 | 1350 | 80 |
| | FS | Best | 16.7 | 0.20 | 0.45 | 1.6 | 150 | 20 |

| | | | | | | | | |
|--|---------|---------|------|------|------|------|-------|----|
| FTO/ZnO/ZnO NW/Perovskite/Spiro-OMeTAD/Au | RS | Average | 14.6 | 0.19 | 0.45 | 1.3 | 130 | 30 |
| | | Best | 17.9 | 0.21 | 0.44 | 1.7 | 220 | 20 |
| | FS | Average | 17.9 | 0.20 | 0.43 | 1.5 | 170 | 20 |
| | | Best | 24.9 | 0.98 | 0.56 | 13.8 | 19960 | 40 |
| FTO/SnO ₂ /Perovskite/Spiro-OMeTAD/Au | RS | Average | 24.1 | 0.97 | 0.57 | 13.3 | 9470 | 40 |
| | | Best | 21.9 | 0.94 | 0.45 | 9.3 | 520 | 50 |
| | Average | | 21.6 | 0.93 | 0.44 | 9.1 | 700 | 50 |

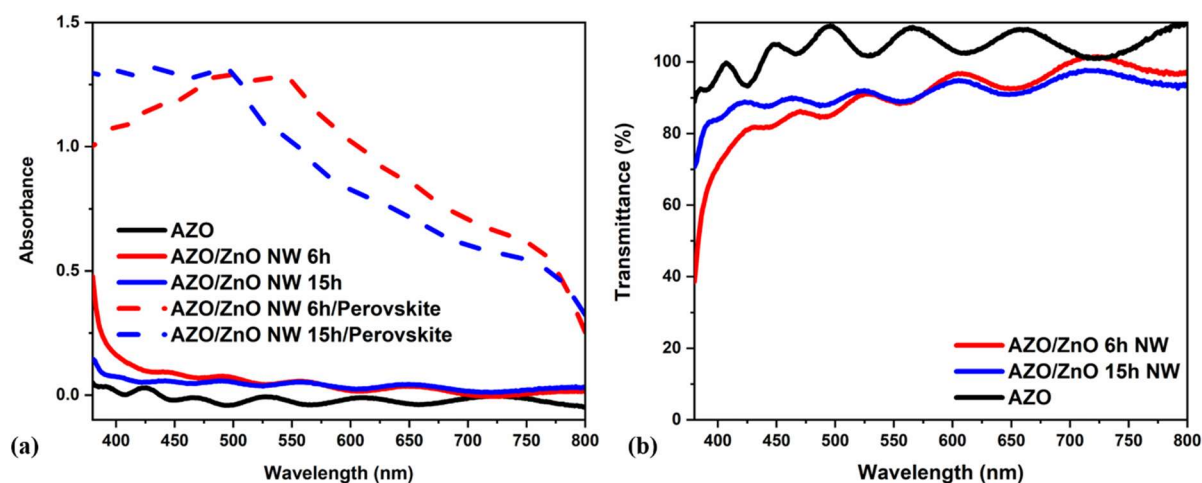


Figure S2. Recorded UV-visible absorbance (a) and transmittance (b) spectral response for ZnO NWs (6h and 15 h) grown on AZO substrate.

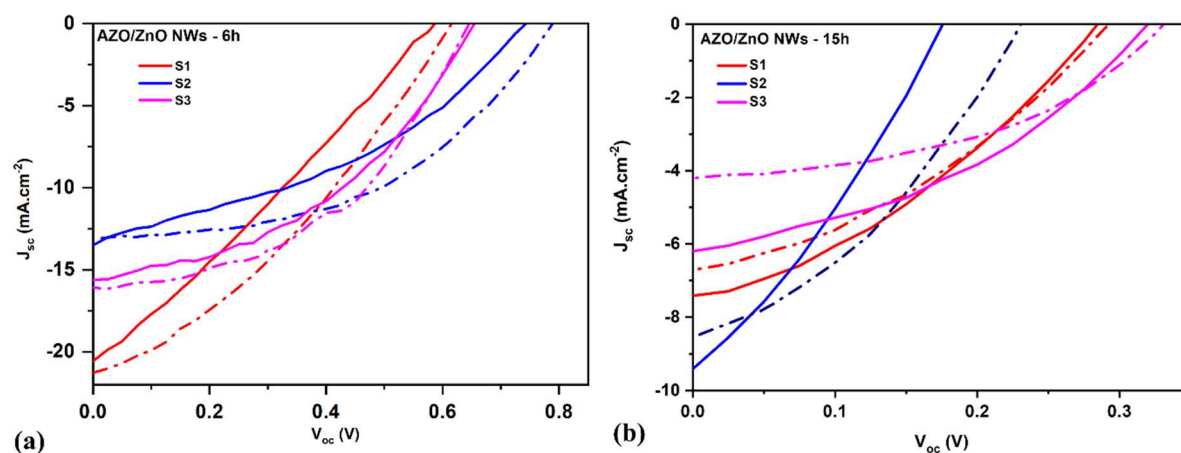


Figure S3. Comparison of several same batch device J-V characteristics of (a) AZO/ZnO NW (6h) and (b) AZO/ZnO NW (15h) solar cells, respectively.

Table S2. Photovoltaic parameters of perovskite solar cells fabricated as a function of ZnO NW array growing time (i.e., 6h and 15h).

| Growth time | Device | J _{sc} (mA.cm ⁻²) | V _{oc} (V) | FF | PCE (%) | R _{sh} (Ω) | R _s (Ω) |
|-------------|--------|---|------------------------|------|------------|------------------------|-----------------------|
| 6h | 1 | FS | 20.2 | 0.58 | 0.28 | 3.3 | 200 |
| | | RS | 20.9 | 0.61 | 0.34 | 4.4 | 90 |
| | 2 | FS | 13.4 | 0.74 | 0.38 | 3.7 | 420 |
| | | RS | 13.1 | 0.79 | 0.48 | 4.9 | 2180 |
| | 3 | FS | 15.6 | 0.65 | 0.43 | 4.3 | 650 |
| | | RS | 16.1 | 0.64 | 0.47 | 4.9 | 1400 |
| Average | FS | 16.4 | 0.66 | 0.36 | 3.8 | 430 | 110 |
| | RS | 16.7 | 0.68 | 0.43 | 4.7 | 1350 | 80 |
| 15h | 1 | FS | 7.0 | 0.28 | 0.37 | 0.7 | 460 |
| | | RS | 6.5 | 0.29 | 0.38 | 0.7 | 560 |

| | | | | | | | | |
|---------|---|----|-----|------|------|-----|------|-----|
| | 2 | FS | 8.4 | 0.17 | 0.35 | 0.5 | 130 | 70 |
| | | RS | 7.9 | 0.23 | 0.40 | 0.7 | 380 | 70 |
| | 3 | FS | 6.1 | 0.31 | 0.40 | 0.8 | 560 | 100 |
| | | RS | 4.2 | 0.32 | 0.46 | 0.6 | 1210 | 130 |
| Average | | FS | 7.2 | 0.25 | 0.37 | 0.7 | 380 | 100 |
| | | RS | 6.2 | 0.28 | 0.41 | 0.7 | 720 | 110 |

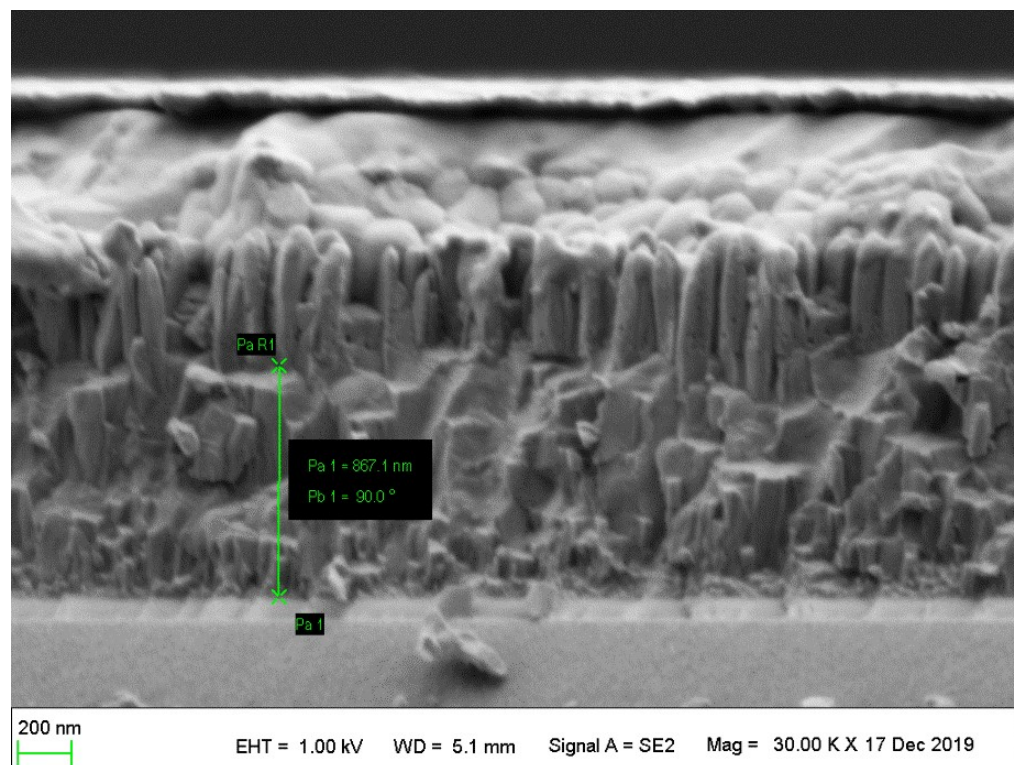


Figure S4. SEM cross-section of a full device based on AZO/ZnO-NW grown for 6h. The image demonstrates a homogeneity of the sandwich structure, with a perovskite solution residing in the ZnO NW layer.

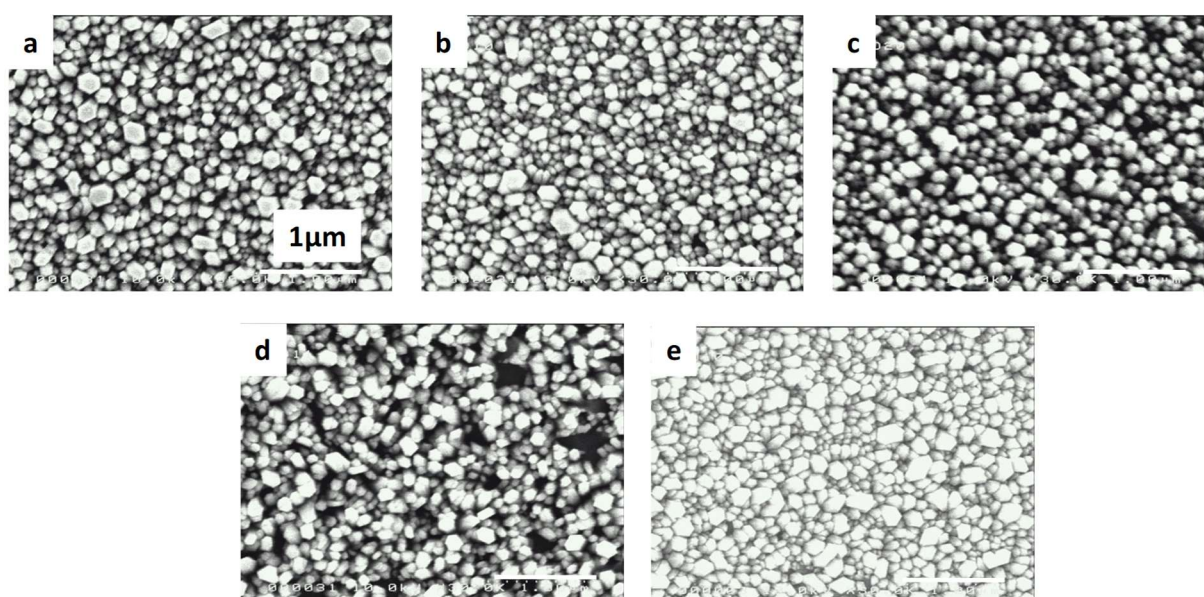


Figure S5. SEM micrographs of ZnO NWs as a function of the $[Zn(NO_3)_2]/[PEI]$ ratio, (a) without PEI, (b) 10, (c) 7.15, (d) 4.5, and (e) 3.85, respectively.

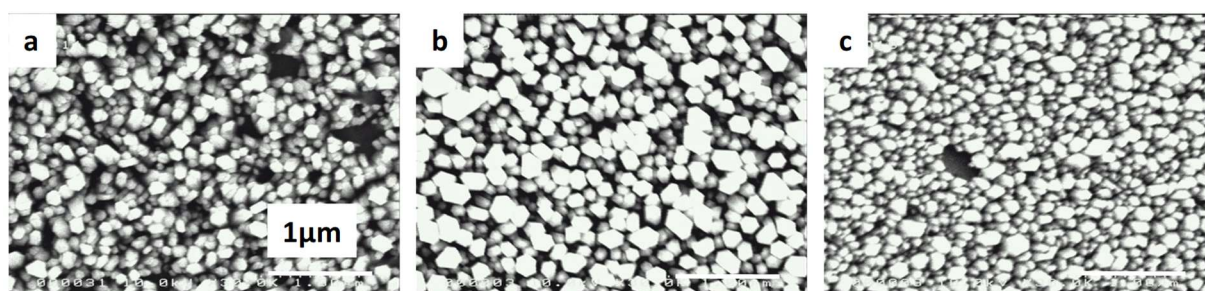


Figure S6. SEM micrographs of ZnO NWs as a function of the $[\text{Zn}(\text{NO}_3)_2]/[\text{HMTA}]$ ratio : (a) 1 ; (b) 1.33 ; (c) 2. The concentration of the $\text{Zn}(\text{NO}_3)_2$ solution is kept constant at 50mM in all cases, and the growing time is fixed at 6h.



Figure S7. SEM micrographs of ZnO NWs as a function of the $[\text{Zn}(\text{NO}_3)_2]$ (a) 20 mM, (b) 35 mM, and (c) 50 mM, respectively.

Table S3. Summary table of the length, diameter, apparent density, and void fraction of ZnO NWs as a function of different conditions.

| | C_1 Zn mM | C_2 HMTA mM | C_1/C_2 | C_3 PEI mM | C_1/C_3 | L (μm) | d (nm) | D NW/μm ² | Void fraction % |
|---------------------------------------|----------------|------------------|-----------|-----------------|-----------|--------|--------|----------------------|--------------------|
| Zn (50mM), HMTA, PEI (1,1,300). 6h | 50 | 50 | 1 | 5 | 300 | 0.4 | 127 | 53 | ~28 |
| Zn (50mM), HMTA, PEI (1,1,300). 15h | 50 | 50 | 1 | 5 | 300 | 1.3 | 165 | 29 | ~58 |
| Zn (50mM), HMTA, (1,1). 6h | 50 | 50 | 1 | -- | -- | 0.3 | 131 | 59 | ~36 |
| Zn (50mM), HMTA, PEI (1,1,10). 6h | 50 | 50 | 1 | 5 | 10 | 0.3 | 135 | 59 | ~37 |
| Zn (50mM), HMTA, PEI (1,1,7.15). 6h | 50 | 50 | 1 | 7 | 7.15 | 0.4 | 147 | 49 | ~44 |
| Zn (50mM), HMTA, PEI (1,1,4.5). 6h | 50 | 50 | 1 | 11 | 4.5 | 0.5 | ~125 | 58 | ~45 |
| Zn (50mM), HMTA, PEI (1,1,3.85). 6h | 50 | 50 | 1 | 13 | 3.85 | 0.2 | 150 | 50 | ~28 |
| Zn (50mM), HMTA, PEI (1,1.33,4.5). 6h | 50 | 37.5 | 1.33 | 11 | 4.5 | 0.5 | 125 | 58 | ~36 |
| Zn (50mM), HMTA, PEI (1,2,4.5). 6h | 50 | 25 | 2 | 11 | 4.5 | 0.3 | 101 | 76 | ~37 |
| Zn (35mM), HMTA, PEI (1,1.33,4.5). 6h | 35 | 26.6 | 1.33 | 7.77 | 4.5 | 0.3 | 117 | 57 | ~46 |
| Zn (20mM), HMTA, PEI (1,1.33,4.5). 6h | 20 | 15 | 1.33 | 4.44 | 4.5 | 0.25 | 109 | 58 | ~43 |

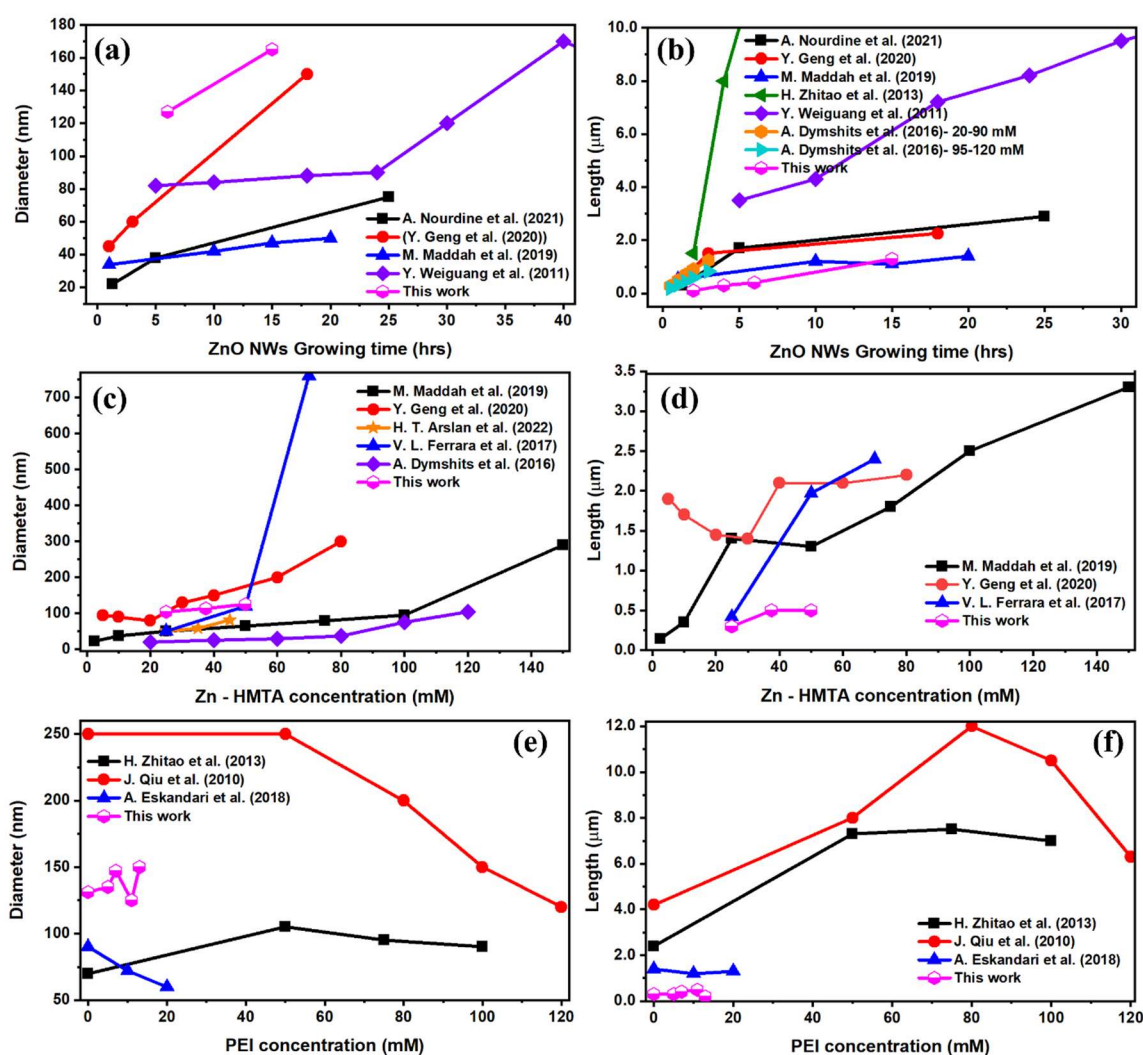


Figure S8. Published reports related to the ZnO NW properties, especially NW length and diameters. Comparison of NW diameters and lengths (a and b) based on growing time, (c and d) based on Zn – HMTA concentration, and (e and f) based on PEI concentration, respectively.

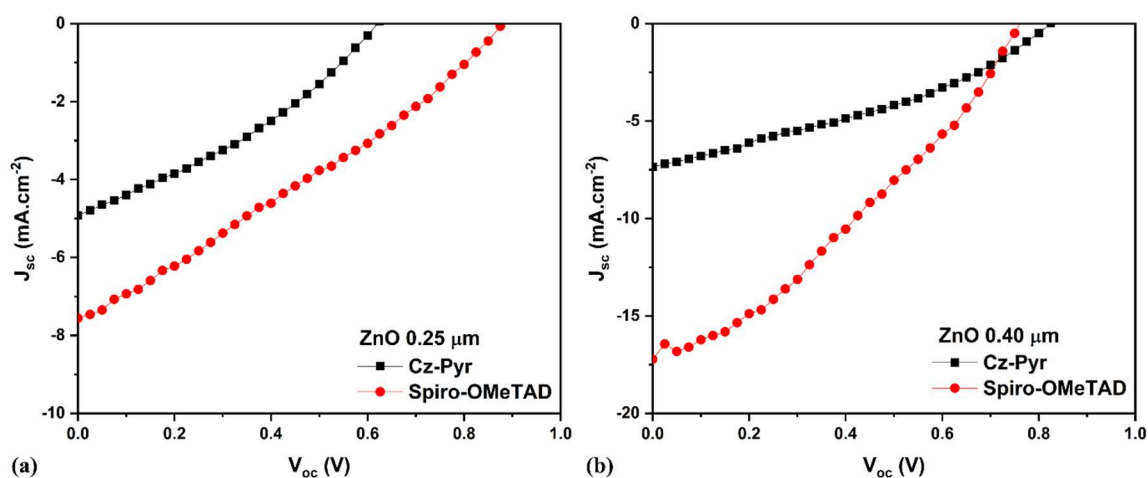


Figure S9. J–V characteristics of perovskite solar cells (best device) fabricated with two different HTLs (Spiro-OMeTAD and Cz-Pyr) using two different NWs (a) ZnO 0.25 μm and (b) ZnO 0.40 μm, respectively.

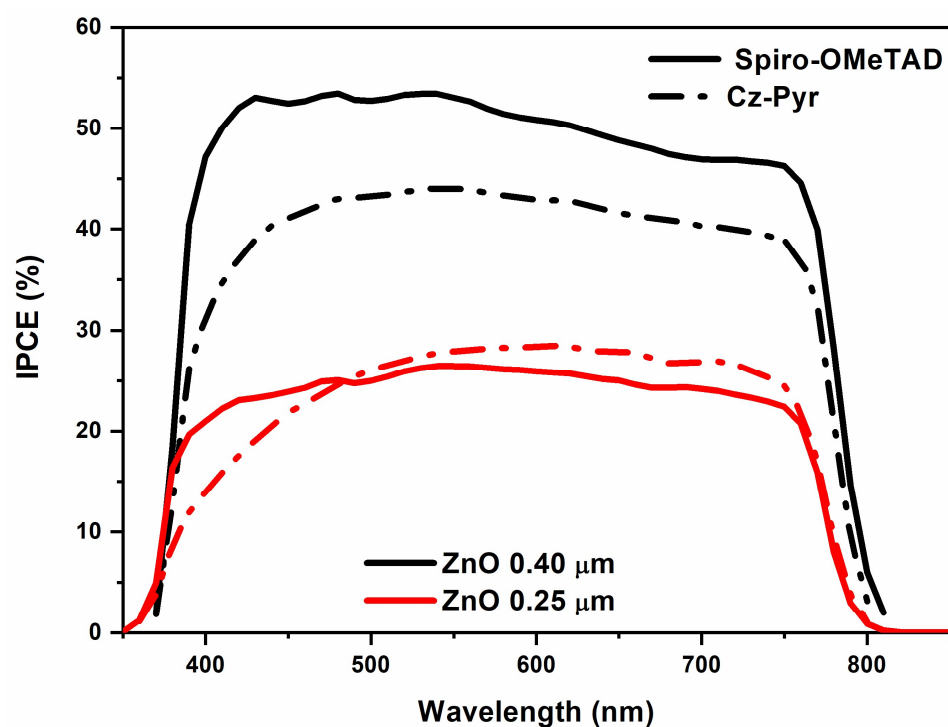


Figure S10. IPCE spectra for the champion solar cells with two different NWs based devices (ZnO 0.40 μm and ZnO 0.25 μm) using two different HTLs (Spiro-OMeTAD and Cz-Pyr), respectively.

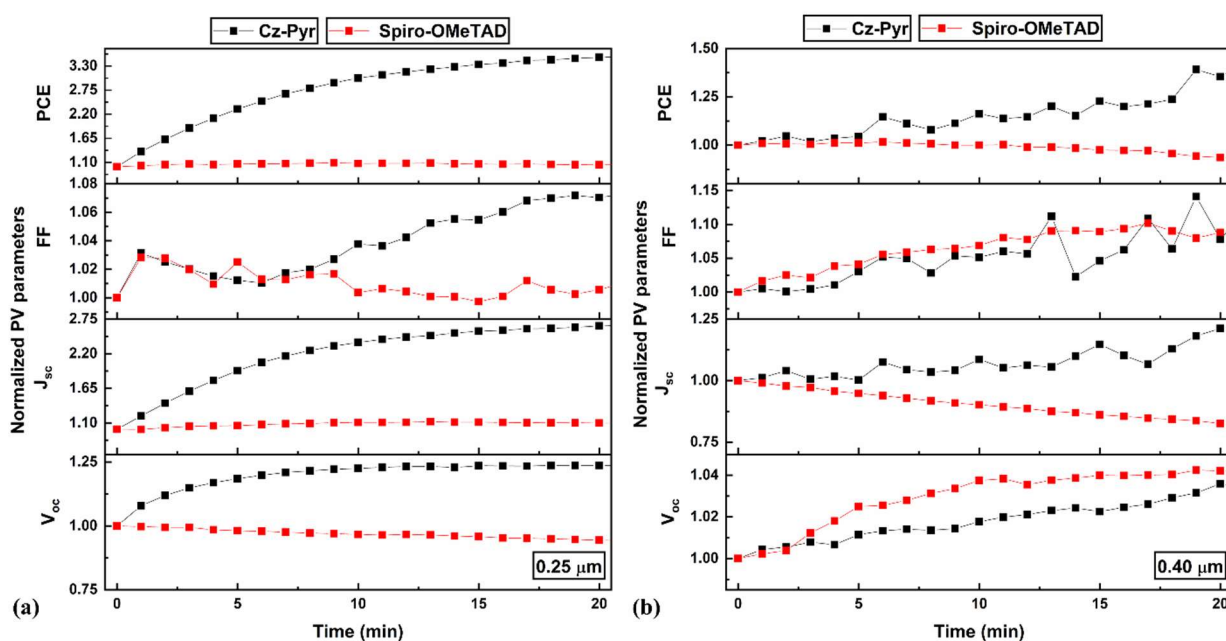


Figure S11. Preliminary aging test of the ZnO NWs (ZnO 0.25 μm (a) and ZnO 0.40 μm (b)) based devices along with two different HTLs (Spiro-OMeTAD and Cz-Pyr), respectively.