Supporting Information for

ZrO_2/TiO_2 Electron Collection Layer for Efficient Meso-Superstructured Hybrid Perovskite Solar Cells

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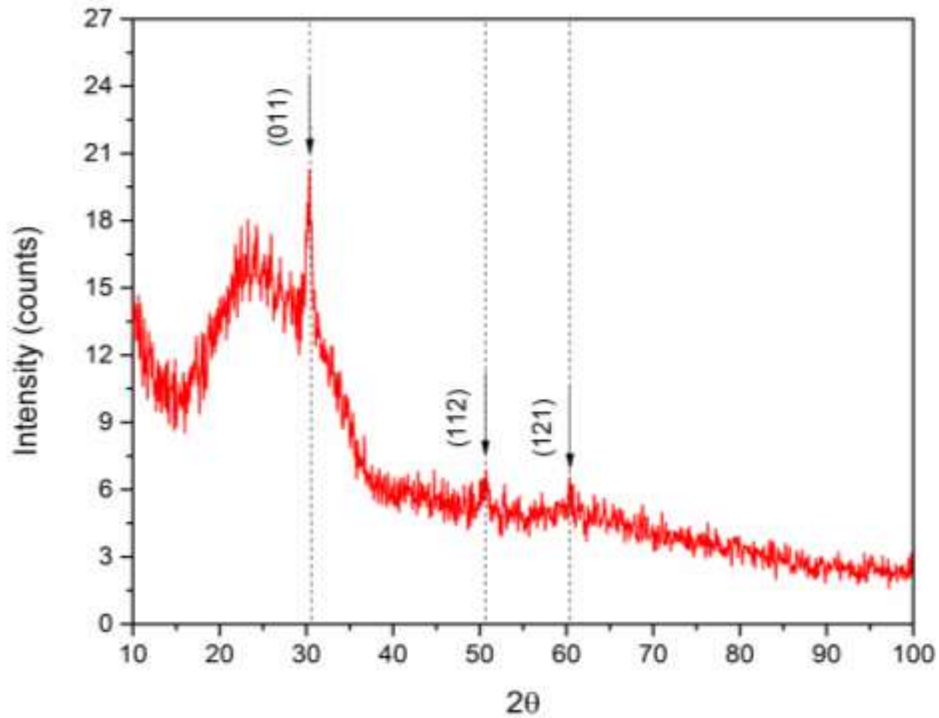

Figure S1. XRD diffractogram of the ZrO_2 film.

Figure S1 shows a broad band (with low intensity) between 15 and 35 may be due to a certain fraction of very small nanocrystsals. Peak width fitting of the sharp and broad peaks indicates crystal sizes of 38.4 nm and 10.5 nm respectively. With respect to small crystals, normally high temperatures are needed to obtain tetragonal zirconia , however since phase transformations in a nanostructured system is linked to crystal size and hence the specific surface area, the energy/surface area ratio is lower than a micro or millimetric structure, needing lower temperatures to reach the desired phase transformation[1, 2]. Garvie demonstrated that under similar conditions to those we have used here (precipitation and calcination temperature), the fabricated zirconia crystallizes completely in a tetragonal phase, with the absence of other crystal phases. Complementary, in this scenario the crystal size is expected to be between 17 and 30 nm. Considering our XRD patters and the work of Shkula and Garvie, it is highly likely that our films are composed of tetragonal zirconia nanocrystals with a range of size from 17 to 30 nm, which it is very similar to the obtained value from peak width fitting.

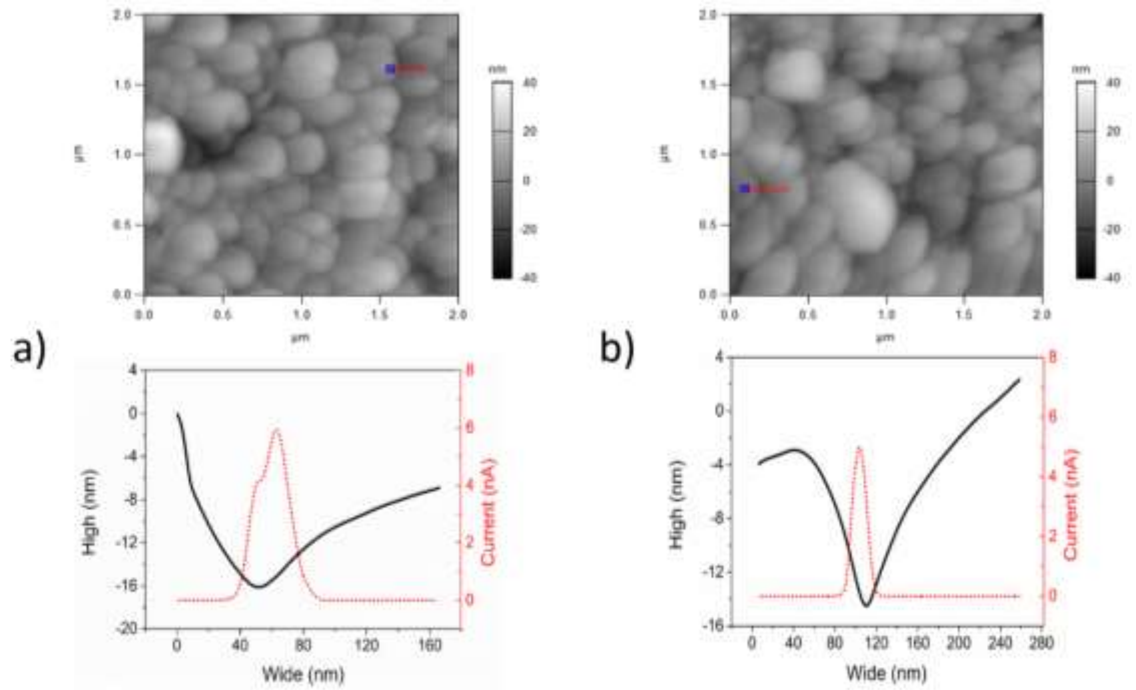

Figure S2. AFM images, morphology and current profile for the pinholes found in the a) TiO_2 and b) ZrO_2 thin layer.

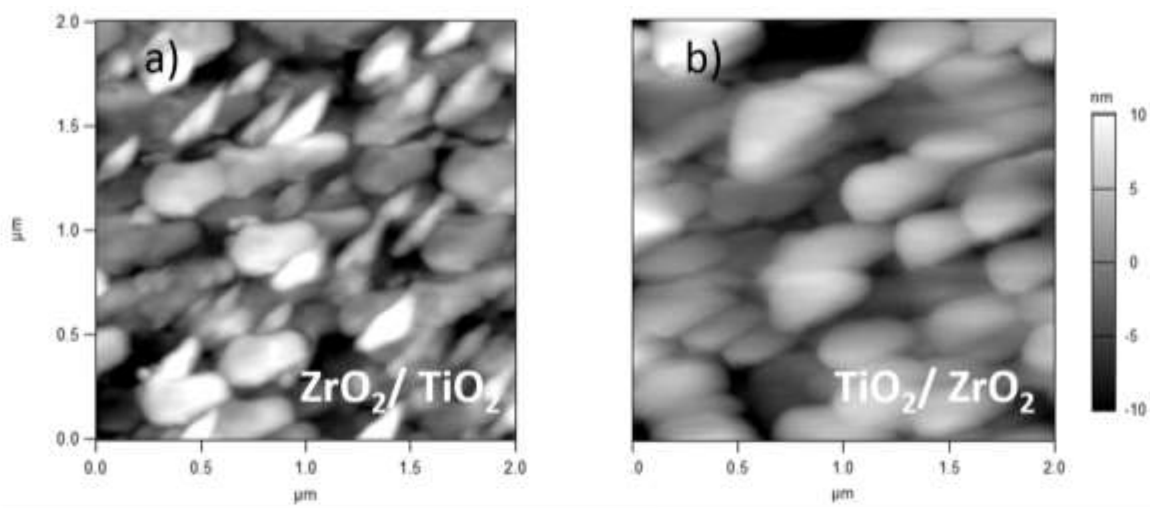

Figure S3. Morphology of the electron collection bi-layers studied in the meso-superstructured perovskite solar cell. a) Zirconia-titania and b) Titania-zirconia thin layer on top FTO.

REFERENCES

1. Shukla, S.; Seal, S., Mechanisms of Room Temperature Metastable Tetragonal Phase Stabilisation in Zirconia. *Int. Mater. Rev*. **2005**, 50 (1), 45-64.

2. Garvie, R. C., The Occurrence of Metastable Tetragonal Zirconia as a Crystallite Size Effect. *J. Phys. Chem.* **1965**, 69 (4), 1238-1243.