Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Highly Conductive, Optically Transparent, Low Work-Function Hydrogen-doped Boron-doped ZnO Electrodes for Efficient ITO-Free Polymer Solar Cells

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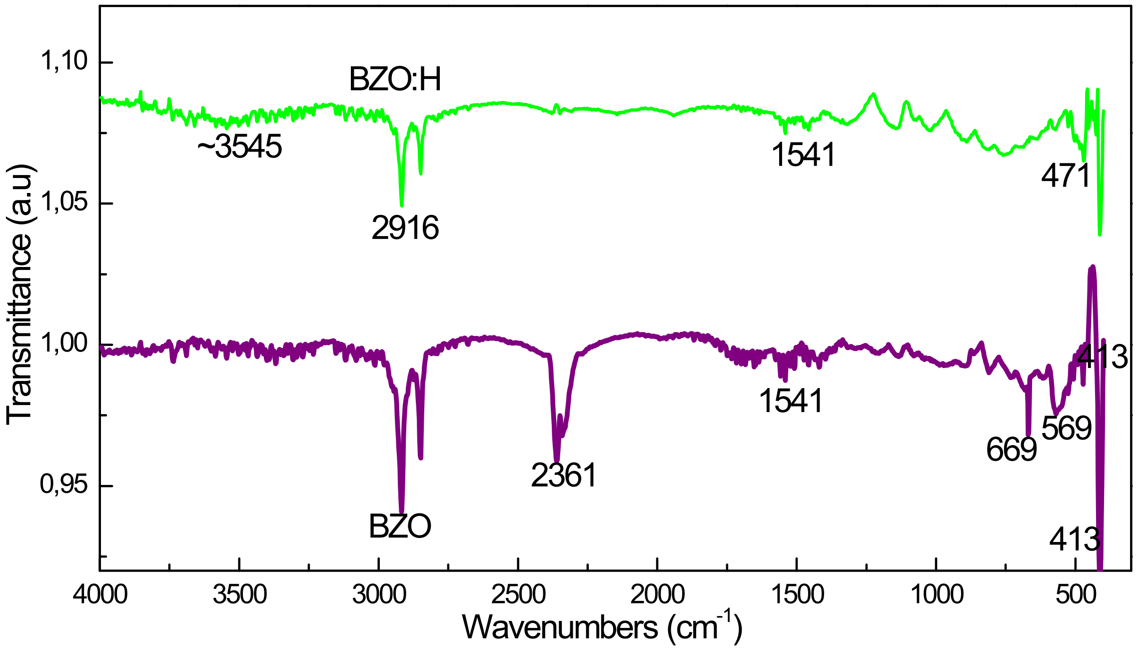
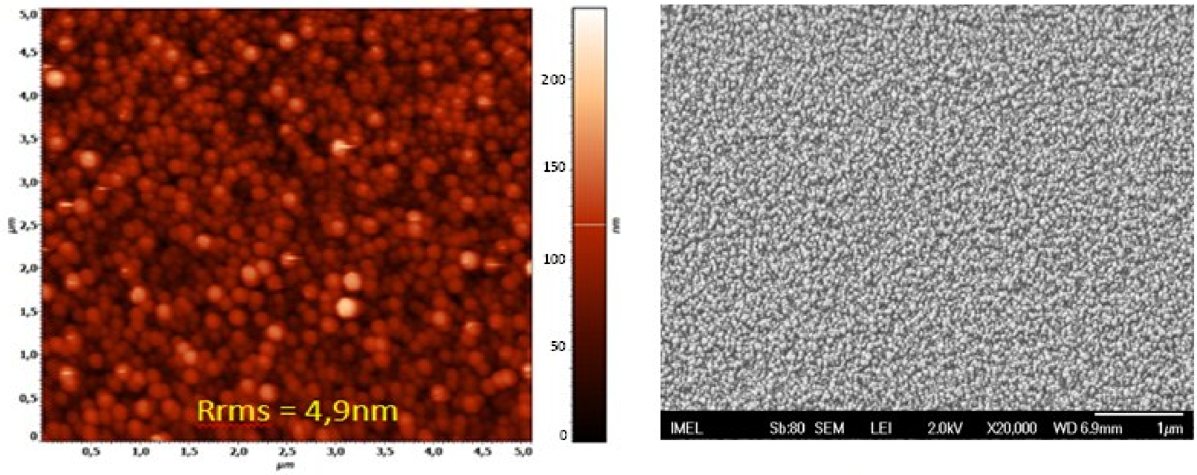
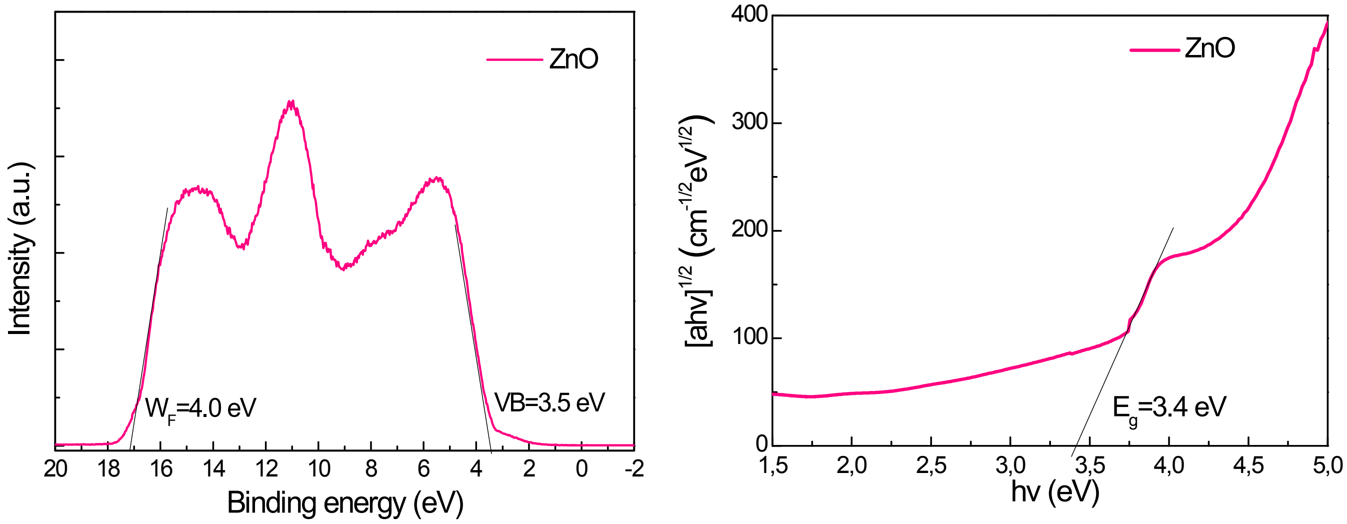


Figure S1. FTIR study of as-deposited and H-annealed BZO films (2% B content). The as-deposited BZO film presents a sharp peak at 413 cm^{-1} (slightly blue shifted in comparison to the band at 408 cm^{-1} reported in literature) attributed to the characteristic Zn−O stretching band of the hexagonal wurtzite ZnO structure.[1,2] It also appears a broad band at 569 cm^{-1} ascribed to other Zn−O stretching modes of wurtzite structure. The large band at 2361 cm^{-1} is ascribed to CO_2 from the atmosphere adsorbed by the metallic cations. Upon H_2 annealing the BZO film presents a decrease in the intensity of the characteristic wurtzite Zn−O bond at 413 cm^{-1} (which is also blue shifted) indicating decrease in the concentration of those structures. Also, a large red shift of the band attributed to other Zn-O stretching modes of wurtzite structure (569→ 471 cm^{-1}) is shown indicating considerable weakening of those bonds. A very significant result is also the appearance of a broad band at ~ 3545cm^{-1} attributed to stretching of O−H bonds.[3] Thus, upon H_2 thermal treatment the ZnO film is hydrogenated, in the sense that it contains -OH groups within its structure.



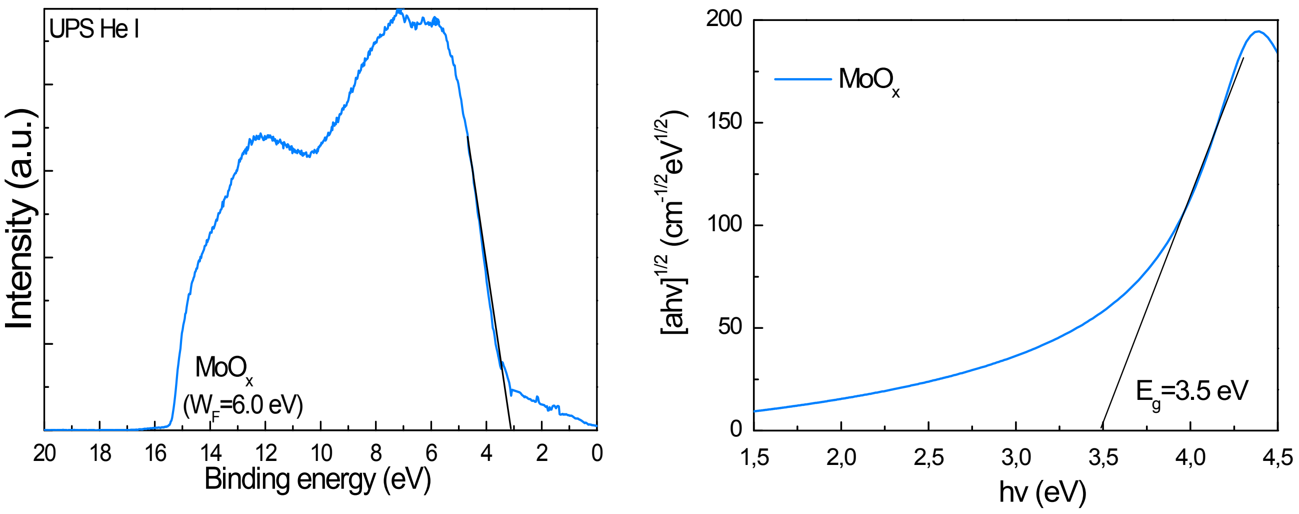
(a) **(b)**

Figure S2 (a) Atomic Force Microscopy (AFM) 2-D and (b) SEM topographies of ZnO films (40 nm thick) derived via a sol-gel method deposited on BZO:H substrates. These films exhibit a short and dense rod-like morphology which is beneficial for the device operation, as it was previously demonstrated by our group.[6]



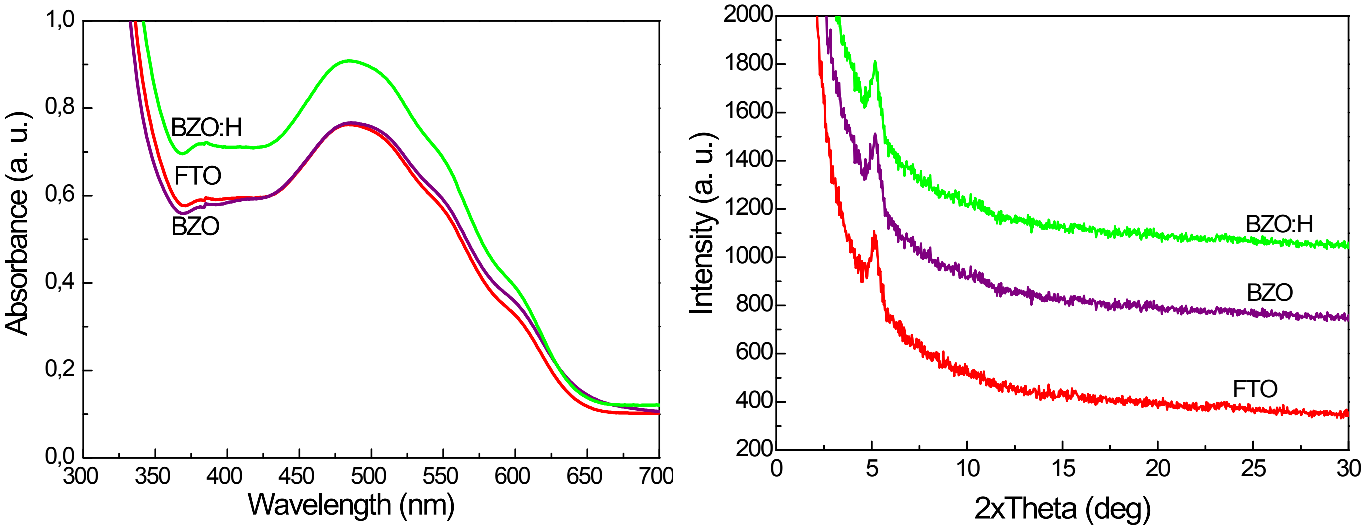
(a) **(b)**

Figure S3. (a) UPS spectrum and (b) tauc plot (as derived from UV-vis absorption spectrum) of 40 nm gol-gel derived ZnO films. According to these spectra the ionization energy of ZnO is -7.5 eV, the energy bandgap is 3.4 eV and the conduction band minimum is placed at -4.1 eV.



(a) **(b)**

Figure S4 (a) UPS spectrum and (b) Tauc plot, as derived from absorption measurements, of a MoO_x film with a thickness of 20nm for the estimation of work function, ionization energy and optical energy band gap.



(a) **(b)**

Figure S5. (a) UV/vis absorption spectra and (b) XRD diffraction patterns of 100 nm P3HT:$PC_{71}BM$ films deposited on different TCO layers. Although the XRD patterns of P3HT:$PC_{71}BM$ films deposited on different TCO substrates exhibited great similarities, the difference of the absorption spectrum of the film deposited on BZO:H substrate is evident. This may be attributed to the better optical transparency of the BZO:H substrate when compared to the BZO and FTO ones.

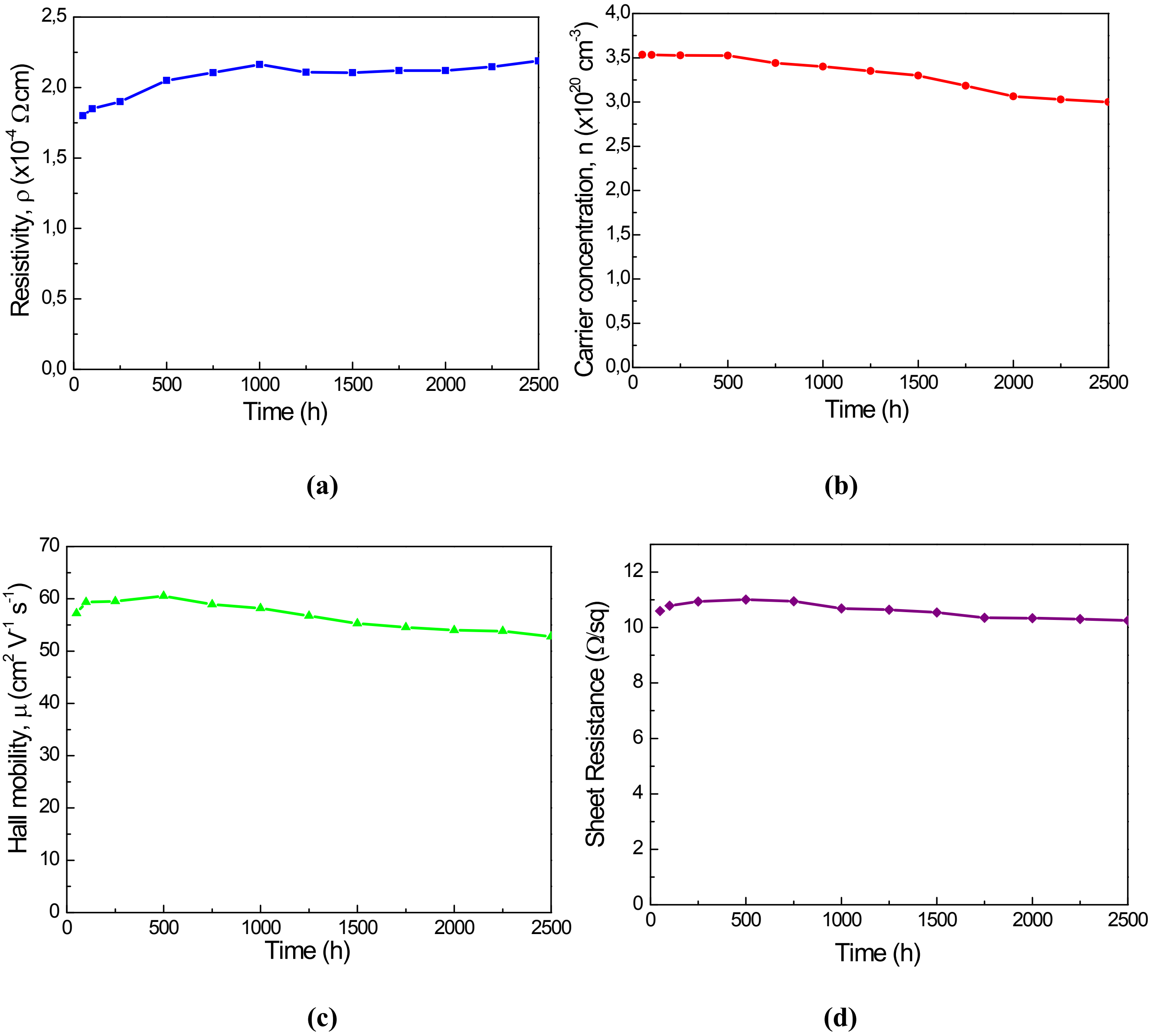
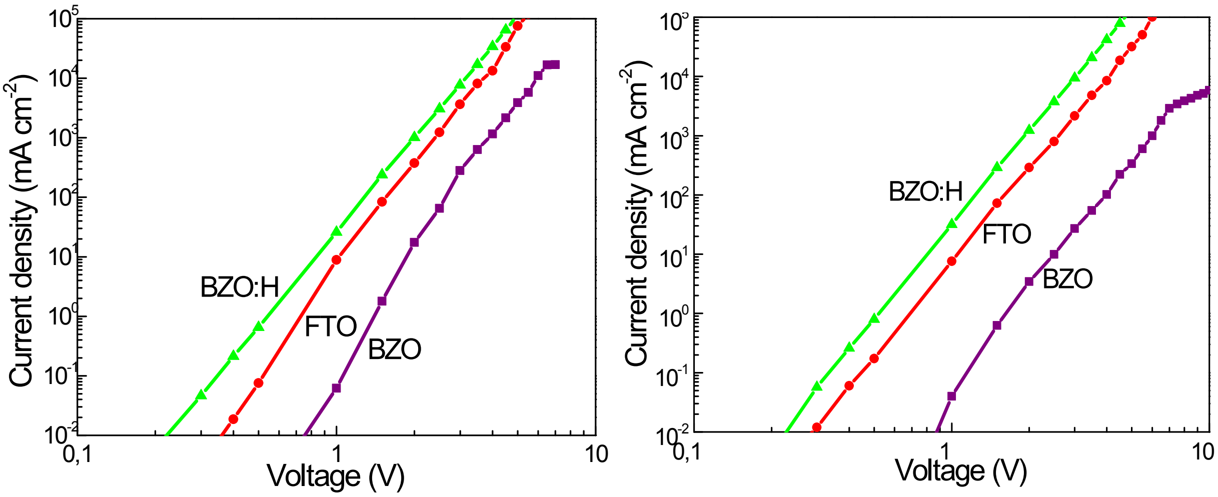


Figure S6. Stability study of BZO:H films. Variation with time of: (a) resistivity, (b) carrier concentration, (c) Hall mobility and (d) sheet resistance of BZO:H films.



(a) **(b)**

Figure S7 Electron only (a) PCDTBT:$PC_{71}BM$ and (b) PTB7:$PC_{71}BM$ based devices with the structure: BZO or BZO:H or FTO cathode electrode/ZnO/active layer/MoO_x/Al.

References

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