Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information for

Hydrogenated under-stoichiometric tungsten oxide anode interlayers for efficient and stable organic photovoltaics

M. Vasilopoulou[*,1], A. Soultati[1], D. G. Georgiadou[1], T. Stergiopoulos[1], L. C. Palilis[2], S. Kennou[3], N. A. Stathopoulos[4], D. Davazoglou[1], P. Argitis[1]

[1]*Institute of Advanced Materials, Physicochemical Processes, Nanotechnology and Microsystems (IAMPPNM), National Center for Scientific Research "Demokritos", 153 10 Aghia Paraskevi Attikis, Athens, Greece.*

[2]*Department of Physics, University of Patras, 26500 Patras, Greece*

[3]*Department of Chemical Engineering, University of Patras, 26500 Patras, Greece*

[4]*Department of Electronics, Technological Educational Institute (TEI) of Piraeus, 12244 Aegaleo, Greece*

*To whom correspondence should be addressed: mariva@imel.demokritos.gr

Additional Figures and text

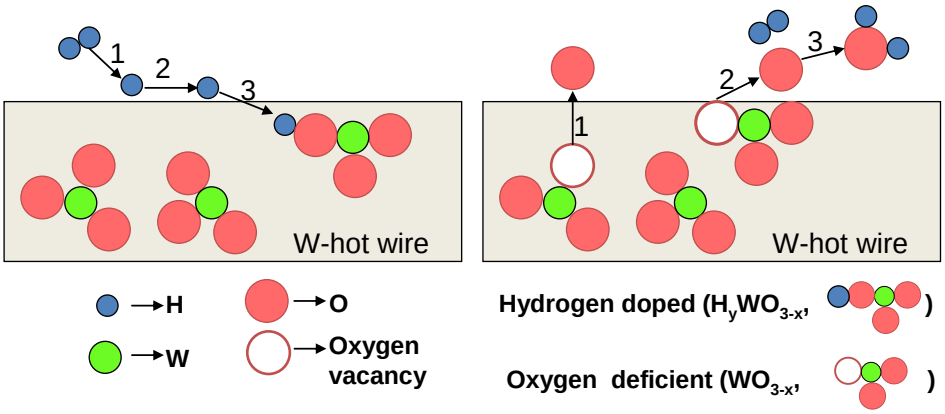

Figure S1. (a) Illustration of the hydrogenation and oxygen vacancies formation mechanisms: The deposition of tungsten oxides by heating a W wire in O_2 environment resulted in the formation of stoichiometric WO_3. When deposited in reducing environment (i.e. containing hydrogen), the obtained materials are under-stoichiometric. In particular, when deposited in nitrogen environment containing a small amount of atomic hydrogen, an oxygen-deficient tungsten oxide (WO_{3-x}) is obtained. In this material oxygen vacancies are generated because of the lack of oxygen in the deposition environment. Through heating the W wire in H_2 environment, hydrogen atoms generated through dissociation of H_2 molecules in the vicinity of the hot-filament are inserted within the WO_3 lattice and are chemically bonded with the lattice (terminal) oxygens. The material obtained in this case is the hydrogenated (hydrogen-doped) H_yWO_{3-x}.

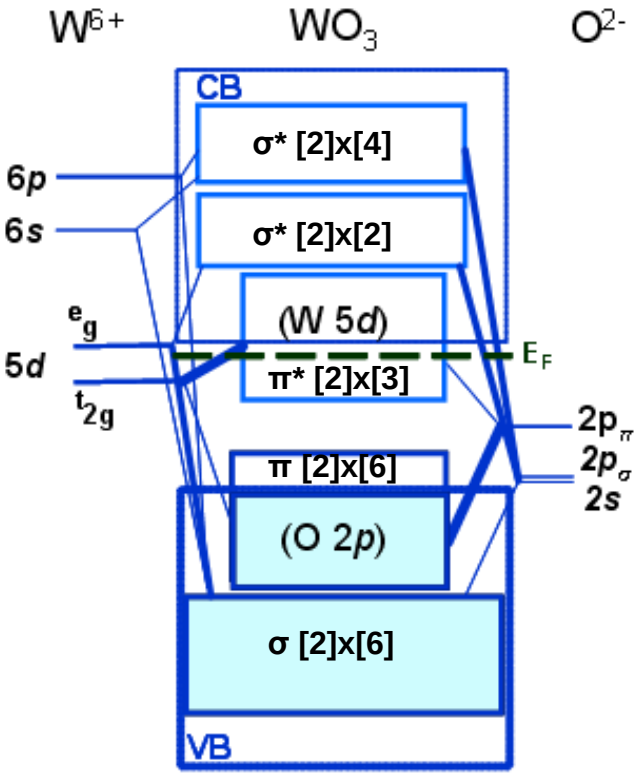

Figure S2. Schematic representation of the band structure of WO_3 according to Goodenough's model for Re_2O_3.[1-4] In a discrete WO_6 unit the W 5d orbitals with e_g symmetry overlap with six sp hybrid orbitals of the oxygen atom to give a set of six bonding σ and six antibonding σ^* molecular orbitals. In the extended lattice, the discrete energy levels arising from this unit structure will broaden into bands. The W 5d orbitals with the lower t_{2g} symmetry can overlap with three of the surrounding oxygen p_π orbitals per octahedron to form bonding π and antibonding π^* bands. The π and σ bands are filled and constitute the valence band separated by a large gap (3.15 eV in our case, Figure S3) from the conduction band constituted of π^* and σ^* bands. The conduction band is empty in WO_3, so this material is a wide bandgap semiconductor, practically an insulator.

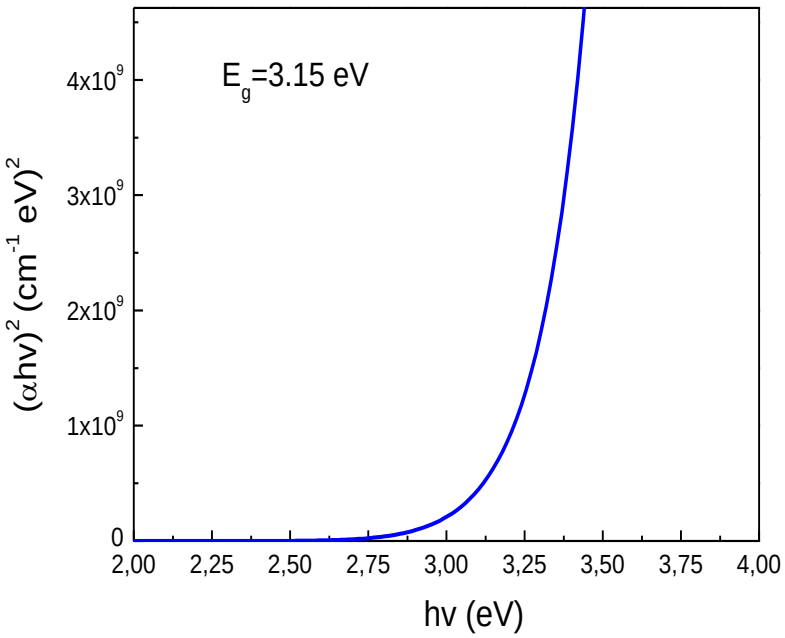

Figure S3. Tauc plot derived from absorption measurements for a 10 nm thick WO_3 film: Stoichiometric WO_3 films that were deposited in O_2 environment exhibit an optical bandgap of approximately 3.15 eV, as calculated from the Tauc plot derived from UV-vis absorption spectroscopy measurements (i.e., the intercept of the tangent in the plot of $(\alpha h\nu)^2$ *versus* $h\nu$ - α is the absorption coefficient - with the $h\nu$ axis gives the bandgap energy).

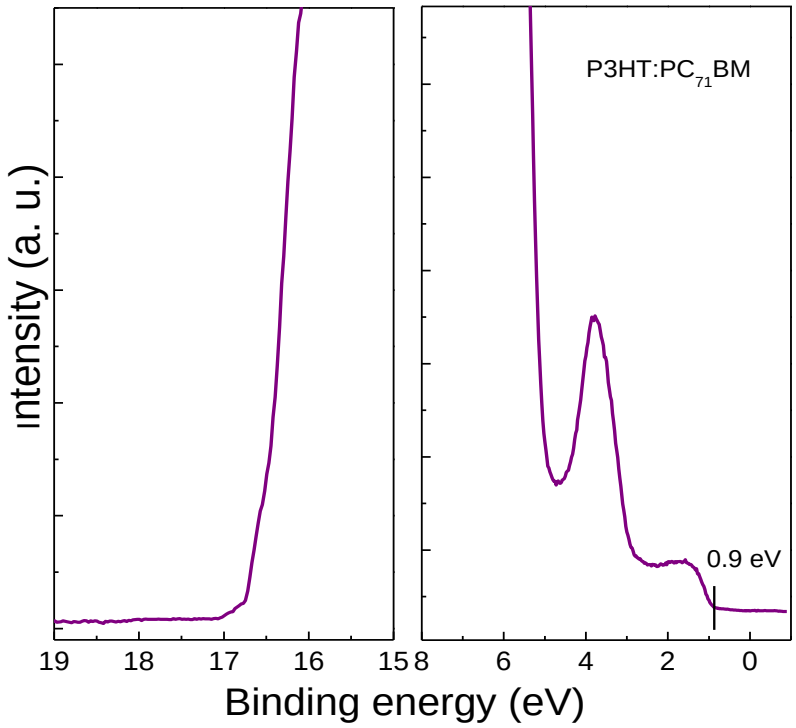

Figure S4: UPS spectra of P3HT:$PC_{71}BM$ film (1:0.8% w/w) with a thickness of *ca.* 20 nm: a HOMO value of 0.9 eV and a W_F of about 4.4 eV can be extracted from these measurements for the P3HT component, resulting in an ionization energy, IE=5.3 eV, in accordance with the literature.[5]

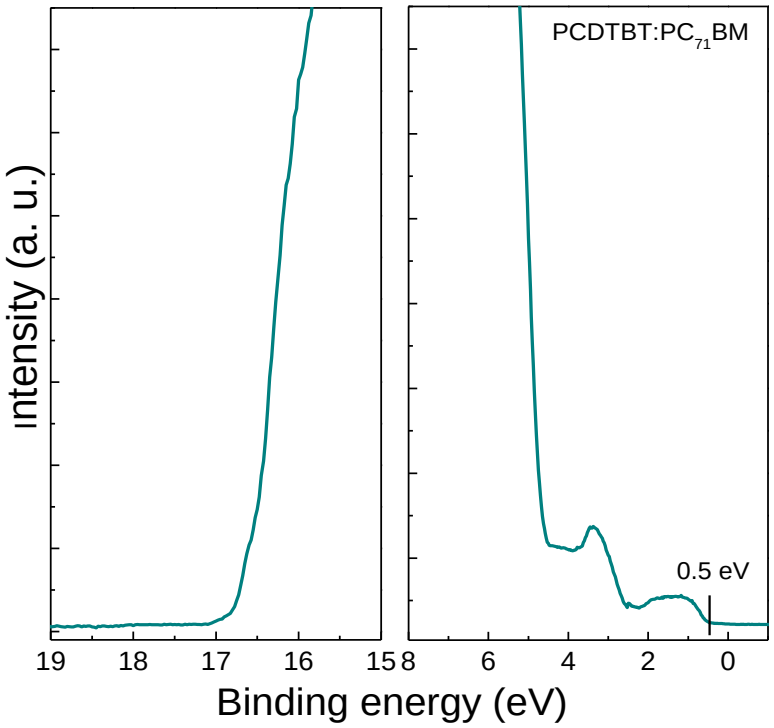

Figure S5: UPS spectra of PCDTBT:$PC_{71}BM$ film (1:4 % w/w) with a thickness of *ca.* 20 nm: a HOMO value of 0.5 eV and a W_F of about 4.5 eV can be extracted from these measurements for the PCDTBT component, resulting in an IE=4.95 eV, in accordance with the literature.[6]

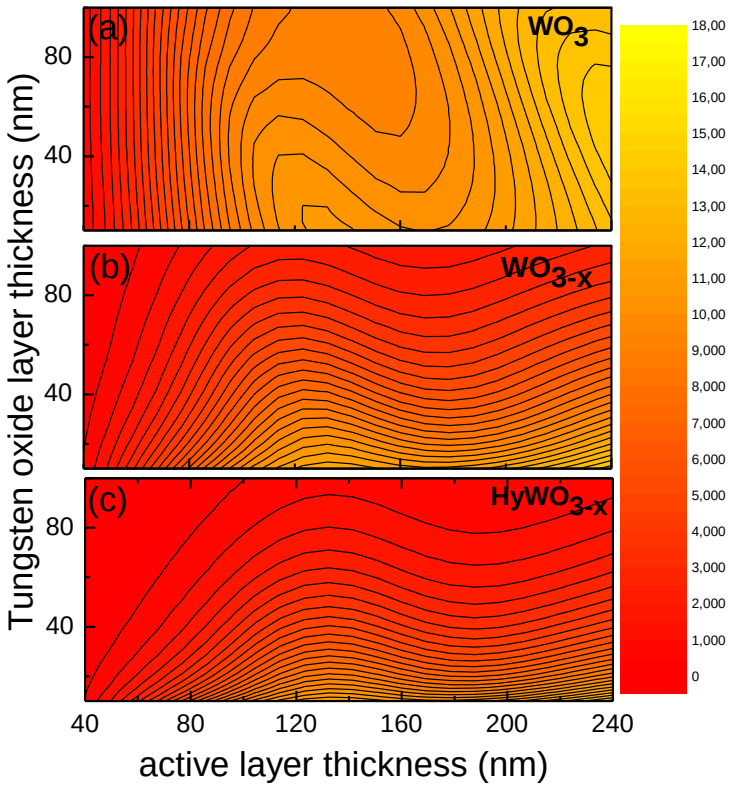

Figure S6 The variation of J_{sc} (vertical bar) as a function of both active layer and tungsten oxide layers' thickness (contour plots)**:** we performed optical measurements (we measured the real and imaginary part of the refractive indices) and carried out simulations to calculate the distribution of the overall photocurrent with the variation of the thicknesses of both the active layer and the tungsten oxide films. The short-circuit photocurrent density of each OPV device under normal light incidence can be calculated by using a transmission line model.[7] In ref. 7 the model has been proposed and used for the evaluation of the WO_3 thin layer, acting as a spacer between the photoactive layer and the aluminium electrode. Herein, the tungsten oxide has been placed between the ITO and the photoactive layer, acting as a hole collector layer. From the obtained data it can be clearly seen that optical effects are not very significant in our devices, where the active layer's thickness is nearly 100 nm and the tungsten oxide layer is about 10 nm. As a matter of fact, both under-stoichiometric tungsten oxides, and especially the hydrogen-doped one, are probably inferior optical spacers than the stoichiometric one.

References

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