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Supplementary Material



Figure S1. SEM image of the triangular shaped sample tip. The X-Ray path through the sample, indicated by the red arrow, is about $100 \ \mu m$.



Figure S2. AFM ($15\mu m * 15\mu m$) image of the ITO substrate surface and line profile extracted in correspondence of line1 is reported.



Figure S3. EDXR patterns of the pristine (black line) and aged (red line) states of the reference device on the left and the GO-BHJ device on the right side respectively. For the reference device the oscillations at lower q-values correspond to the Al signal, while at higher values the fringes related to the PEDOT:PSS are also observed. For the Go-BHJ the AL electrode signal only was detected.



Figure S4. XRF layer-wise analysis tracking Indium K_{α} fluorescence line for the pristine (A) and aged (B) state of the PEDOT:PSS-HTL reference device.



Figure S5. Comparison of FTIR spectra of the glass/ITO/GO film in its pristine (black line) and aged (red line) state. The pristine state shows the spectral markers of the free water: a broad H_2O band (O–H sym-asym. stretch at 3280 cm⁻¹). In the aged state no spectral markers of free water are present. Vibrations at 2800-2950 cm⁻¹ are due to –CH2CH3 alkyl stretchings, hint of a possible GO reduction. Indeed, at lower wavenumebrs, the intensity loss of the C-O stretching band at 1116 cm⁻¹ and of the C=O stretching at 1735 cm⁻¹ suggests that reduction may have occurred.



Figure S6. IPCE and absorbance spectra of PEDOT:PSS, GO and rGO-based devices, (a), (b) before and after (c), (d) 20 h and (e), (f) 40 h solar illumination. The insets represent the absorption decay for each HTL material (PEDOT:PPS, pr-GO and GO respectively) in the three different time points (0, 20 and 40 hours).