Supporting Information

for

A scanning probe microscopy study of nanostructured TiO_2/poly(3-hexylthiophene) hybrid heterojunctions for photovoltaic applications

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Figure S1a shows a FM-AFM height image obtained in UHV over a 3800 × 400 nm² area astride the step edge between a 200 nm thick nano-structured TiO_2/P3HT-COOH HHJ (right part of the image) and the area of the ITO-glass substrate left uncovered (left part of the image).

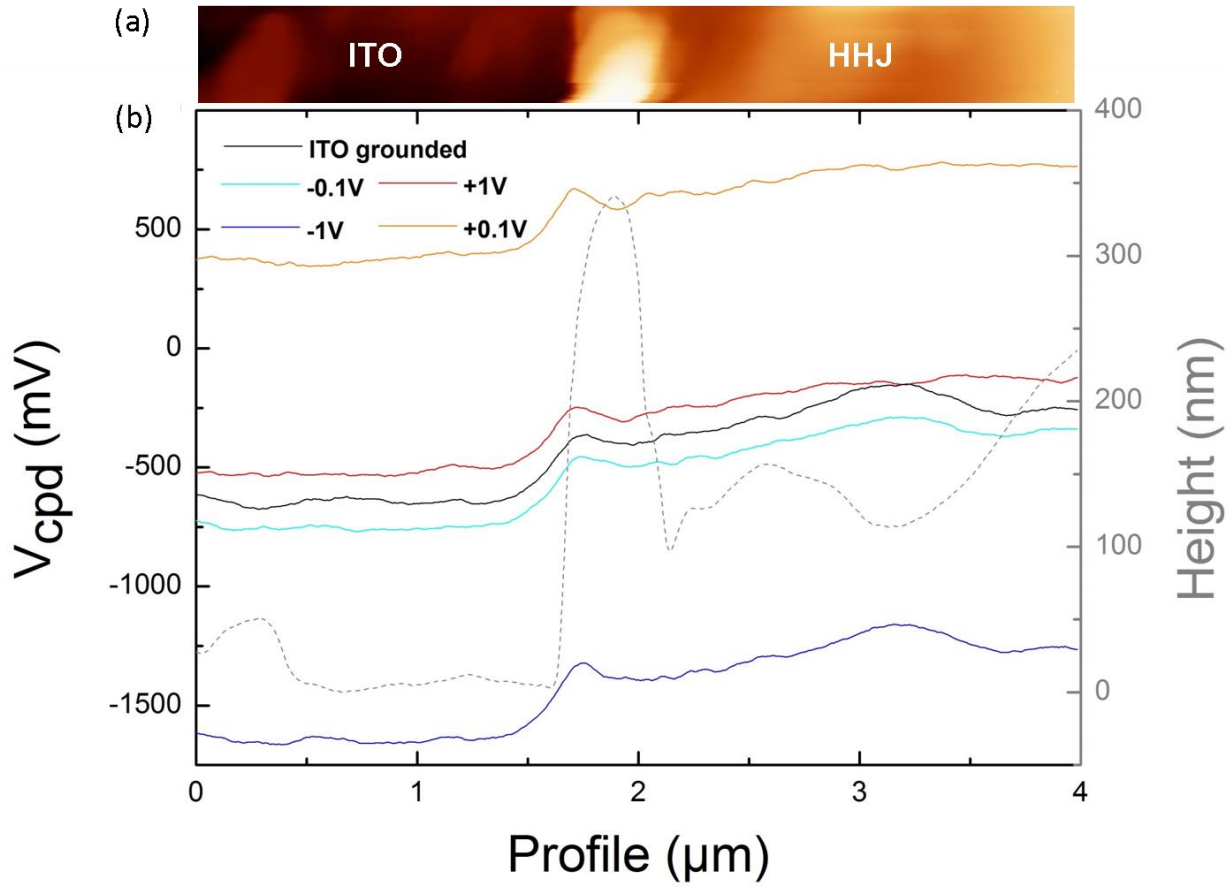

Figure S1: (a) FM-AFM height image in UHV over a 3800 × 400 nm² scan size astride the interface of a 200 nm-thick nano-structured TiO_2/P3HT-COOH HHJ (right part of the image) and the ITO electrode lying below (left part of the image). FM-AFM parameters: -5 Hz of frequency shift setpoint and 50 mV of amplitude setpoint. (b) V_{cpd} profiles extracted from the corresponding V_{cpd} image (along the full length of the scanned area) for different DC sample biases, without illumination, and superimposed to the corresponding height profile. FM-KPFM parameters : frequency and amplitude of the electrical excitation : 958 Hz and 600 mV.

Such a measurement allows observing the V_{cpd} step across the ITO/HHJ step for different biases applied to the ITO electrode. The absence of floating potential is expected to lead to a conservation of the V_{cpd} step, with a global shift of the entire

V_{cpd} profile according to the DC sample bias value (up-shift for positive bias and vice versa). In order to visualize this V_{cpd} step profile for each applied bias, Figure S1b shows cross-sections extracted from the corresponding V_{cpd} image along the total length of the scanned area, at different lines corresponding to different DC sample biases, without illumination. A cross-section extracted from Figure S1a illustrates the typical height profile corresponding to the V_{cpd} cross-sections. The measured amplitude of the V_{cpd} step averaged over the 6 profiles is (405 ± 11) mV. The small standard deviation of the average value of the V_{cpd} step (inferior to 3%) indicates negligible variations of the V_{cpd} step with the magnitude of the applied bias on the ITO electrode. This shows the absence of a floating potential across the ITO/HHJ stacking.

Figure S2 shows the superimposed profiles of the FM-KPFM height and V_{cpd} recorded in UHV along a given scan line over a nano-structured TiO_2 film. The measurement was performed successively with and without illumination. It can be seen that negligible change in the topography appears, ensuring the absence of light-induced artefacts in the topography recording. A very good matching of the V_{cpd} profiles is observed as well: only small discrepancies not exceeding 25 mV are measured between the two curves. This value is negligible in relation to the overall variation amplitude of the V_{cpd} signal across the image. On a more general view, the averaged V_{cpd} values without illumination and upon illumination are (905 ± 58) mV and (890 ± 55) mV, respectively. The difference between the averages is contained within the standard deviation. We can therefore conclude that, if any photovoltaic effect intrinsic to the ITO/ TiO_2 system is present, it is very small.

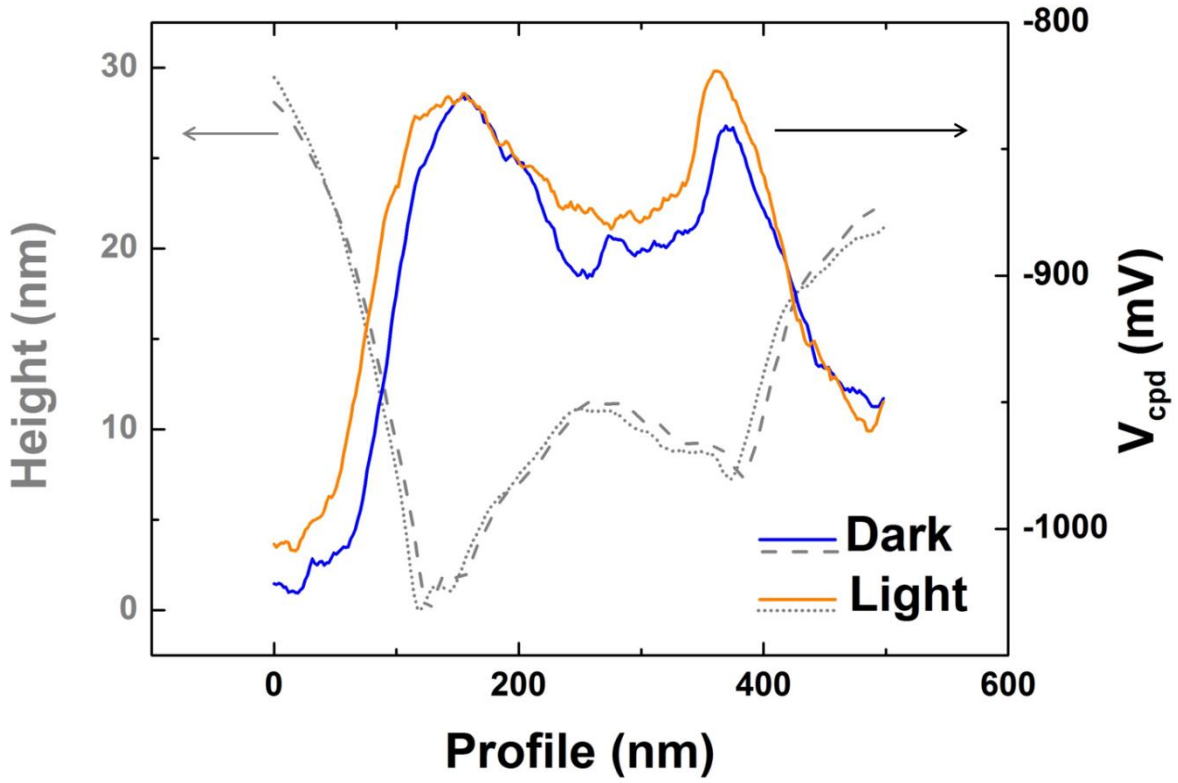

Figure S2: FM-KPFM height and V_{cpd} profiles over a nano-structured TiO_2 film deposited on an ITO electrode, recorded with and without illumination. The measurement was performed in UHV. FM-AFM parameters: -22 Hz of frequency shift setpoint and 40 mV of amplitude setpoint. FM-KPFM parameters: frequency and amplitude of the electrical excitation : 958 Hz and 600 mV.