Supporting Information

Majority Charge Carrier Transport in Particle-Based Photoelectrodes

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S1. Numerical Inter-Particle Charge Transfer Mechanisms

The numerical *I-V* curves of case 3 for varying inter-particle electron transfer velocities are depicted in Figure S1. The inter-particle potential barrier was fixed to 0.0762 V to ensure flat bands at the inter-particle contact. The contributions of the second particle below 0.8 V_{RHE} are not relevant since the onset potential is at ~0.8 V_{RHE} as depicted in Figure S1.a) and b).

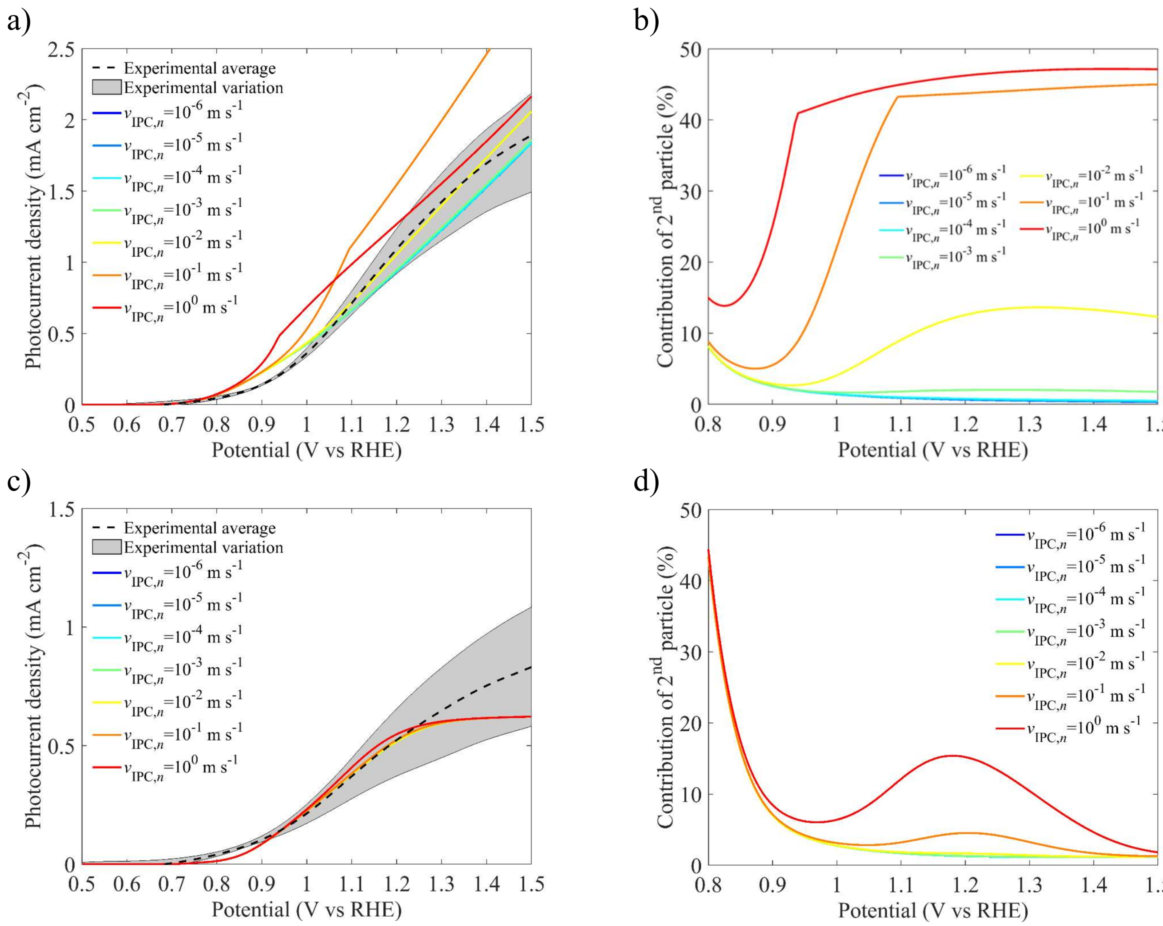

Figure S1. Experimental *I-V* curves of best-LTON PBPE with an average film thickness of 8.43 μm taken from Gaudy et al.[1]. The corresponding numerical *I-V* curves of case 3) for varying inter-particle electron transfer velocities under a) back-side illumination and c) front-side illumination, and the corresponding contribution of the 2nd particle on the right side in b) and d).

S2. Best-LTON Photoelectrodes with 50 nm IrO_x

50 nm of IrO_x were deposited on a best-LTON PE[1] by sputtering at ambient temperature (Alliance-Concept DP 650). The LTON PE with 50 nm IrO_x on top were tested under back illumination only since the IrOx blocks almost completely the light. Figure S2 compares the photocurrent of the same LTON PE before and after IrO_x deposition. As it can be seen, the photocurrent is highly improved, i.e. a relative increase of 67 % at 1.23 V_{RHE}. The LTON PE without IrO_x was freshly prepared when measured. The same LTON PE was then modified with IrO_x to enable direct comparison. However, the performance of LTON PE with IrO_x might be underestimated, since aging effects between the two measurements cannot be excluded. The onset potential is also slightly lowered with IrO_x similar to the numerical prediction[1].

The photoelectrochemical measurements were conducted in a three electrode setup with the LTON PE as working electrode, a Ag/AgCl reference electrode (sat. KCl) and Pt as counter electrode. The electrolytes used was 0.1 M Na_2SO_4 as a buffer solution with pH=13.0±0.2 by adding NaOH. The potential was controlled with a potentiostat (Bio-Logic VSP-300) controlled by EC-lab software and the scan rate for the cyclic voltammetry was 10 mV s^{-1} from 0 V_{RHE} to 1.5 V_{RHE}. The sample was illuminated by the solar simulator VeraSol-2 from Oriel corresponding to AM1.5G[1]. The current density was averaged between forward and backward swept voltage of one sample because of the presence of a hysteresis.

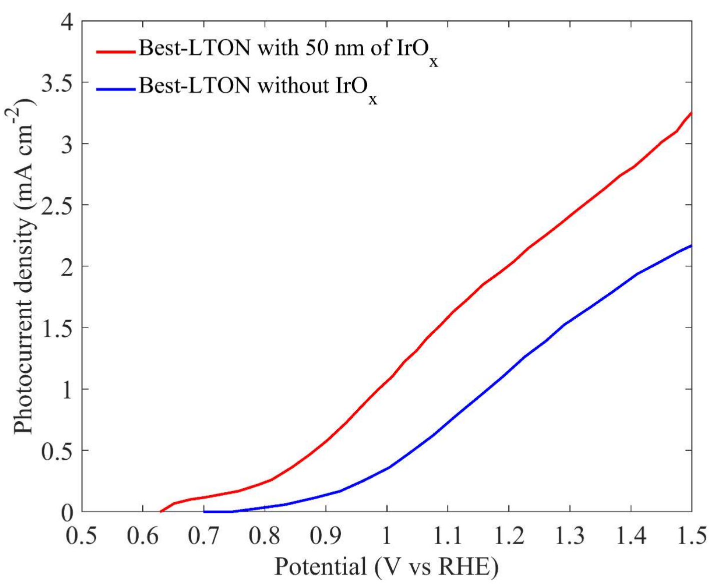

Figure S2. Experimental *I-V* curves of best-LTON PE with and without a 50 nm layer of IrO_x in 0.1 M Na_2SO_4 at pH=13.0±0.2 by adding NaOH.

References

(1) Gaudy, Y. K.; Dilger, S.; Landsmann, S.; Aschauer, U.; Pokrant, S.; Haussener, S. Determination and Optimization of Material Parameters of Particle-Based LaTiO2N Photoelectrodes. *J. Mater. Chem. A* **2018**, *6*, 17337–17352.