

Graphene-based Hole Selective Layers for High-efficiency, Solution-processed, Large-area, Flexible, Stable Hydrogen-Evolving Organic Photocathodes

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Hydrogen-evolving photocathode architectures based on solution-processed organic semiconductors are now emerging as promising low-cost alternatives to the ones using crystalline inorganic semiconductors based on Si, oxides and III-V alloys.[1] In particular, regio-regular poly(3-hexylthiophene-2,5-diyl) (rr-P3HT), the workhorse of the organic photovoltaics, has been recently exploited in bulk heterojunction (BHJ) configuration with phenyl-C61-butyric acid methyl ester (PCBM) for photocathodes reaching photocurrents above 8 mA cm⁻² at 0 V vs. RHE.[2-3] The overall performances of these photocathodes strongly depend on the presence of the electron (ESL) and hole (HSL) selective layer.[1-3] While TiO₂ and its sub-stoichiometric phases are consolidated materials used as ESL, the currently used HSL materials (e.g., MoO₃,[1] CuI,[2] PEDOT:PSS,[3] WO₃[4]) suffer electrochemical degradation under hydrogen evolution reaction (HER)-working conditions.[4] This limits the life-time of the photocathodes, lasting from several minutes to about few hours.[1-4] In this work, we demonstrate the potentiality of 2D materials[5] as HSL.[6,7] In particular, both solution-processed GO and rGO are proposed as HSL to boost efficiency and durability of rr-P3HT:PCBM-based photocathodes. We demonstrate record high performances concerning all-solution-processed rr-P3HT:PCBM-based photocathodes. In fact, our devices show

photocurrent at 0 V vs. RHE ($J_{0V \text{ vs RHE}}$) of -6.01 mA cm⁻², onset potential (V_0) of 0.6 V vs. RHE, ratiometric power-saved efficiency (ϕ_{saved}) of 1.11% and operational activity of 20 hours. Moreover, our (r)GO-based photocathodes are demonstrated to be effective in different pH environment ranging from acid to basic, showing $J_{0V \text{ vs RHE}}$ exceeding 1 mA cm⁻². This is pivotal for their exploitation in tandem configurations, where photoanodes operate only in restricted electrochemical conditions. Furthermore, we demonstrate the up-scaling feasibility of our approach by fabricating a large-area (9 cm²) flexible (onto ITO-PET substrate) photocathodes, with remarkable $J_{0V \text{ vs RHE}}$ of 2.8 mA cm⁻², V_0 of 0.45 V vs. RHE and ϕ_{saved} of 0.31%.

References

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Figures

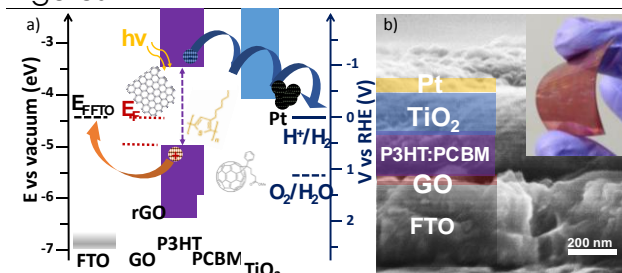


Figure 1: a) Scheme of the materials energy band edges position and b) its high-resolution cross-sectional SEM image. The inset to b) shows a photograph of a large-area (9 cm²) photocathode fabricated on flexible ITO-PET substrate.