PROBING THE PHOTOPHYSICS OF LEAD-HALIDE HYBRID PEROVSKITE JUNCTIONS UNDER VERY INTENSE OPTICAL IRRADIANCE

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Laser-assisted Time-Resolved Scanning Electron Microscopy and Photoluminescence were jointly applied to show that the recovery dynamics of photophysics in lead-halide hybrid perovskite junctions, at irradiances up to 500 suns, crucially depends on selective contacts type.
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1. Introduction

Hybrid lead halide perovskites are most highly-performing absorber materials for advanced thin film solar cells, with certified record values of Power Conversion Efficiency higher than 25% [1]. They are also extremely appealing for high concentrated photovoltaic applications at high levels of optical irradiance [2,3] and as light emitting devices [4]. Actually, the photophysics of photovoltaic perovskite junctions under high irradiance is quite complex, due to soft and defective crystalline structure, leading to material instabilities. Therefore, to assess the impact of intense illumination on the performances and long-term reliability of hybrid perovskites is of major importance and still an open research challenge.
Dynamical characterizations of *surface photovoltage* (SPV) and photoluminescence (PL) may help to unveil the photophysics of the system. We apply novel laser-assisted Time-Resolved Scanning Electron Microscopy (TR-SEM) [5] as a fast way to visualize dynamical SPV and we couple it to *in-situ* quasi-steady state PL to study long-term evolution of charge dynamics in $MAPbI_3$ films, excited by intense optical irradiance at 500 suns, in dependence on the kind of selective contacts.

2. Results and Discussion

$MAPbI_3$ films were deposited by the two step interdiffusion method on charge selective contacts, namely electron-transport-layer (ETL) compact TiO_2 and hole-transport-layer (HTL) PEDOT:PSS, respectively, and illuminated at 500 suns equivalent intensity.
In the absence of any external bias, a large positive SPV builds up in both systems at the free surface of the films with a turn-on time of seconds and a much slower decay time of tens of minutes and up to hours. Mixed electron-ionic conduction and defect formation and migration -triggered and driven by strong optical absorption- can be at the origin of the phenomenon. However, different photo-polarization dynamics in the two cases unveils a major influence of the surface and the diverse role played by electrons and holes in $MAPbI_3$ photochemistry depending on the substrate.
Specifically, $MAPbI_3$/PEDOT:PSS films behaves more as a p-type semiconductor, with reversible photo-excited polarization effects and a fast and reversible quenching of PL, consistently with the hypothesis of optically activated non-radiative and defect-mediated charge recombination paths. $MAPbI_3/TiO_2$ films are more n-type, feature much slower and non-reversible PL quenching, photo-induced inhomogenous and semi-permanent space-charge fields, with very long-lasting local modifications in the work function at the grain level.
The results are discussed in the hypothesis that different types of photogenerated charge traps are activated by high optical irradiance in either systems, while the TiO_2 layer may act as a photocatalyst of chemical reactions leading to degradation of the perovskites and to a permanent polarization of the film.
Jointly performed TR-SEM and PL confirm that the specific nature of the charge selective contact and related interface crucially affect the optoelectronic response of $MAPbI_3$.
The results of characterizations suggest that films grown on PEDOT:PSS are more robust in view of high-irradiation applications, while in the case of TiO_2 even in the absence of morphological surface damage, physico-chemical degradation may locally occur in the bulk and at the contact interface, definitely altering the photo-physical response of the material and deserving further investigations.

References

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