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Design and Characterizations of Perovskite Solar Cells

Hung-Yu Hsu¹ and Eric Wei-Guang Diao¹

¹ National Chiao Tung University.
Department of Applied Chemistry and Institute of Molecular Science,
1001 University Road, Hsinchu 30010, Taiwan
Phone: +886-3-5131524, E-mail: diau@mail.nctu.edu.tw

Abstract

Both n-type and p-type perovskite solar cells will be introduced based on varied structural configurations of the devices. The excitonic relaxation dynamics of perovskite on different metal oxide films were recorded based on femtosecond spectral techniques and a relaxation mechanism is given to rationalize the observed dynamics.

1. Introduction

Generating cost effective and environment benign renewable energy remains a major challenge for scientific development. Solar energy, which is abundant and sustainable, has attracted enormous effort in research and development for many years. A major advance in the development of inorganic sensitizers of new types occurred in 2012: Park and Grätzel reported thin-film solid-state solar cells attaining PCE 9.7 % with a methyl ammonium lead-iodide perovskite sensitizer, $\text{CH}_3\text{NH}_3\text{PbI}_3$, in a mesoporous TiO_2 film (thickness 0.6 μm).¹ This perovskite sensitizer has a bandgap 1.5 eV and V_{OC} of this perovskite-sensitized solar cell was much greater than that of a dye-sensitized solar cell, rendering this photovoltaic system promising for further investigations. At nearly the same time, Snaith and co-workers reported a similar perovskite, $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$, that served as light absorber for mesoscopic thin-film solid-state solar cells to attain PCE 10.9 %, ² for which the mesoporous Al_2O_3 film served as a scaffold to replace the n-type TiO_2 electron-transporting layer. Because of the insulating characteristic of Al_2O_3 , the electrons generated from the excited perovskite sensitizer cannot inject into the Al_2O_3 layer; the photo-induced electrons were then transported in the perovskite layer on the surface of the mesoporous Al_2O_3 film. As a result, much greater V_{OC} (> 1.1 V) was attained for such a great photovoltaic performance of an all-solid-state inorganic-organic hybrid solar cell. As there is no n-type component for electron transport in the Al_2O_3 -based solar cells, the perovskite layer might exhibit a bi-functional feature acting as both light absorber and electron carrier; it is no longer a solar cell of sensitized type.

In 2013, Snaith and co-workers reported a significantly enhanced PCE 12.3 % for perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ solar cells with the same device structure based on Al_2O_3 .³ The development of all solid-state mesoscopic solar cells

has reached a new milestone when Grätzel,⁴ Snaith,⁵ Kelly⁶ and their co-workers reported the perovskite-based solar cells with PCE exceeding 15 % using spiro-OMeTAD as hole transporting material. The great discovery of the perovskites as novel photovoltaic materials has hence opened a new channel for the development of third-generation solar cells with advantages of great efficiency, cheapness, ease of processing and great endurance.

2. Results and Discussion

Recently, we have demonstrated that perovskite solar cells using mesoporous NiO nanocrystals as p-contact electrode material in a device configuration NiO /perovskite/PCBM attained PCE 9.5 %, giving promising perspective for further development of all-inorganic perovskite-based thin-film solar cells and tandem photovoltaics. To understand the excitonic relaxation mechanism in the perovskite solar cells, in this work we carried out femtosecond fluorescence up-conversion measurements for perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) deposited on thin films of nanocrystalline TiO_2 , NiO and Al_2O_3 upon excitation at 450 nm.

Al_2O_3 , TiO_2 and NiO nanocrystalline films were prepared on glass substrate using spin coating of the dispersive solutions containing the corresponding nanoparticles to attain uniform mesoporous films with thickness ~ 500 nm. The $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer was then deposited on those mesoporous films according to the sequential procedure reported elsewhere.⁴ Femtosecond transient PL spectra were measured upon excitation at 450 nm with the emissions probed at the spectral region 650-810 nm.

The observed excitonic relaxation dynamics were well described by three transient components in a composite consecutive kinetic model with four time coefficients corresponding to (i) hot-hole cooling, (ii) hot-electron relaxation, (iii) cold excitons' surface-state relaxation and (iv) cold excitons' electronic relaxation. The quenching of emission of perovskite was more significant on NiO film than on Al_2O_3 film, and this is understood due to the contribution of the relaxation from the conduction band (CB) to the non-emissive surface state of the cold perovskite excitons being more significant for the former than for the latter. The hole extraction time from perovskite to NiO was estimated at the peak of emission (770 nm) to be ~ 5 ns, which is much slower than that observed for the

perovskite/Spiro-OMeTAD system (0.66 ns observed at 760 nm).⁷ Considering the relatively rapid electron extraction time (0.40 ns) in the perovskite/PCBM film,⁷ perovskite should be a good hole carrier for the p-type NiO-based perovskite solar cells showing remarkable device performance.

3. Conclusions

The present study reports the investigation of the relaxation dynamics of perovskite deposited on TiO₂, NiO and Al₂O₃ films using femtosecond optical gating technique upon excitation at 450 nm. The photoluminescence (PL) transients of the two films observed in the 650 – 810 nm spectral region all feature three wavelength-dependent transient components described in a composite consecutive kinetic model involving the processes of hot-hole cooling, hot-electron relaxation, surface-state exciton relaxation and bulk-state internal conversion. The enhanced quenching of PL of perovskite on NiO with respect to that on Al₂O₃ is due to the exciton relaxation to the non-emissive surface state which is more significant on the NiO film than on the Al₂O₃ film. The present results suggest that perovskite itself can be served as an effective hole transporter after charge separation in the perovskite/PCBM interface. Our investigation thus establishes a concrete kinetic model to understand the excitonic relaxation dynamics of perovskite in varied film configurations.

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