

# Ultrafast Carrier Dynamics in Perovskite Solar Cells under Light Irradiation

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## Abstract

Here we present the implications of energy transfer in photoinduced degradation of perovskite solar cells by discussing the hot carrier relaxation via broadband femtosecond pump-probe spectroscopy.

## Introduction

Lead halide-based perovskite solar cells have drawn considerable interest because of their high efficiency at room temperature. For applications, a major limitation of these systems is their poor stability under ambient conditions and their degradation upon prolonged exposure to heat and sunlight. However, the nature of photo-induced degradation is still unclear. Femtosecond pump-probe spectroscopy has been commonly used for investigation of ultrafast carrier dynamics [1,2].

In this study, we investigate the carrier dynamics of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> with continuous photo-illumination. After light irradiation, the changes in carrier dynamics were clearly observed, which further reveals the mechanism of the degradation of perovskite solar cells under light exposure.

## 2. Results and Discussion

To understand the carrier dynamics of photo-induced degradation in perovskite (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films on TiO<sub>2</sub>), we employed femtosecond transient absorption spectroscopy. The perovskite solar cells were tested under light exposed inside a glove box. The pump pulse can generate the non-equilibrium carriers and the difference absorbance of probe can reveal the ultrafast relaxation processes. Figures 1(a) and 1(b) exhibit the transient difference absorbance spectra at different probing wavelengths before and after the light exposure on perovskite thin films, respectively. The negative parts of difference absorbance in both spectra are related to the photobleach (PB) mechanism. Usually, PB occurs when excited states are over populated or there are valence electron deficiencies, which prevents the interband transitions from valence band to conduction band. The bleach signal decays as carriers recombine or inject into TiO<sub>2</sub> [3]. The negative signal observed after 700 nm in both samples could be related to fluorescent emission from perovskite.

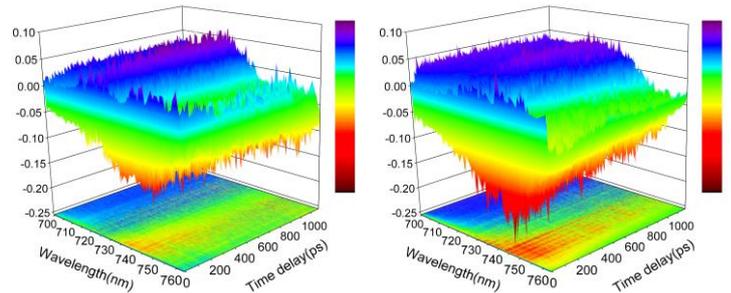


Fig. 1 The transient difference absorbance spectra at different probing wavelengths in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/TiO<sub>2</sub> (a) before and (b) after light exposed.

The transient difference absorbance spectra at each wavelength can be resolved by fitting the following tri-exponential function:

$$\Delta OD = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3} \quad (1)$$

The difference absorbance spectra show several important features which are different between the cases of non-exposed and exposed perovskite thin films. The time constants in non-exposed CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/TiO<sub>2</sub> are  $\tau_1 = 19$  ps,  $\tau_2 = 247$  ps and  $\tau_3 = 4167$  ps while the time constants for exposed CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/TiO<sub>2</sub> are  $\tau_1 = 35$  ps,  $\tau_2 = 245$  ps and  $\tau_3 = 1954$  ps. The shortest exponential decay ( $\tau_1$ ) indicates trap filling at defect sites and grain boundaries. The  $\tau_1$  of exposed-perovskite film is nearly 2 times longer than that of the non-exposed perovskite film. The result indicates the photo-excited carriers in the exposed perovskite film would be significantly trapped in grain boundaries under photo-illuminated degradation. Besides, the photoexcited carriers could transfer from perovskite active layer to TiO<sub>2</sub> layer with time constant  $\tau_2$ . Interestingly, the injection of photo-excited carriers from perovskite active layer to TiO<sub>2</sub> layer is independent on the light exposure.

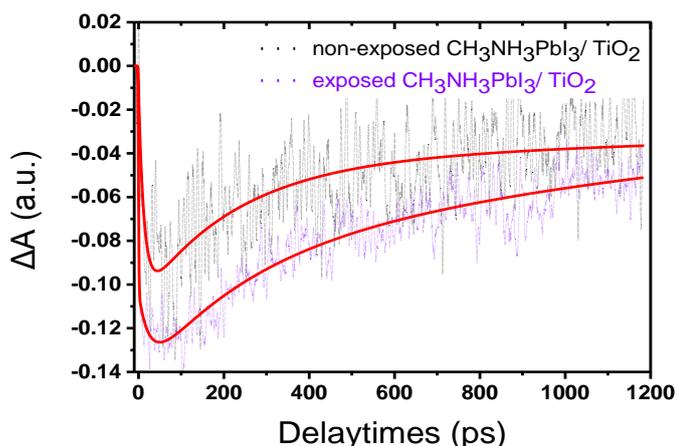


Fig. 2 Time-resolved difference absorbance traces at 750 nm for non-exposed and exposed  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{TiO}_2$  thin films.

Moreover, the negative peak intensity of the exposed perovskite thin film significantly increases (Fig. 1(b)), comparing with that in non-exposed perovskite film. The decay time constant ( $\tau_3$ ) of the non-exposed perovskite film is 4167 ps, which is longer than that (1954 ps) of exposed perovskite film. We propose that the photoinduced degradation generates some trapping sites in the perovskite films, and thus the photoexcited carriers in the exposed perovskite film would be significantly trapped in grain edges to further enhance the nonradiative recombination.

### 3. Conclusions

For applications, it is imperative to fundamentally understand the mechanism of photo-induced degradation in perovskite active layers. In this study, the carrier dynamics of perovskite films under exposure of continuous light illumination have been investigated by broadband femtosecond pump-probe spectroscopy. Through the analyses in time-resolved difference absorbance traces, we found that the intensity of PB increases by 1.5 times in the light-exposed perovskite films. Additionally, the number of grain edges in the light-exposed perovskite films would increase to trap more photoexcited carriers and thus enhance the non-radiative recombination.

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