UV induced degradation in perovskite photovoltaics studied by femtosecond pump-probe spectroscopy

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Abstract

In this work, the ultrafast carrier dynamics for the TiO₂-based perovskite solar cells with and without UV irradiation have been investigated by ultrabroadband femtosecond pump-probe spectroscopy. The experiment results clearly identify a correlation between the electron-hole recombination and UV aging of perovskite solar cells, thus providing profound insight into the driving factors of UV-induced degradation in perovskite solar cells.

1. Introduction

Organic/inorganic hybrid perovskite solar cells have emerged as the most promising candidate for the next-generation photovoltaics. Generally, perovskite solar cell has a planar heterojunction structure, in which the perovskite layer is coated with an electron transporting layer (ETL) in one side and hole transporting layer (HTL) in the other side. The ETL and HTL play vital roles in the perovskite solar cell. It should function as a good extractor and conductor to the generated photocarriers in the perovskite layer, and it should form less recombining interface with the perovskite active layer. Moreover, their stability upon humidity and elongated light exposure also should be resolved. Several efficient transporting materials for electrons were tested and found that the power conversion efficiency (PCE) was elevated using TiO₂ in recent years. However, the perovskite solar cell with TiO₂ as an ETL are very sensitive to UV irradiation [1], which further lead to the degradation in its performance. For instance, the PCE of perovskite /compact TiO₂ solar cell was reduced by 95% under 5 hour UV irradiation in air. It is essential to understand the mechanism of UV-induced degradation in this photovoltaic device. In this study, we used time-resolved femtosecond (fs) pump -probe spectroscopy to investigate the carrier dynamics in perovskite/compact TiO₂ heterojunction solar cell with and without UV irradiation. The experiment results reveal that the electron-hole recombination plays a vital role in the UV-induced degradation of TiO₂-based perovskite solar cells.

2. Results and Discussion

The samples were fabricated on a clean fluorine doped tin oxide glass substrates. The compact TiO_2 film was



Fig. 1 (a) The cross-sectional TEM image and (b) the evolution of current–voltage characteristic curves of the perovskite solar cells consisting of the TiO_2 as an ETL.

prepared according to a standard procedure and a perovskite film was coated on it. The thickness of perovskite and compact TiO₂ were estimated to be 0.85µm and 0.15µm, respectively, from cross-sectional TEM image (see Fig.1(a)). Time-resolved pump-probe studies were performed using a fs Ti:sapphire laser system delivering near-infrared (NIR) pulses. The NIR laser pulses were split into two beams using a beam splitter. One beam is used to generate a second harmonic of 400 nm via BaBiO₃ crystal to pump the samples. The other beam is focused on a sapphire plate to generate a broad visible spectrum, extending from 450 to 760 nm. After pumping, the hot electrons quickly diffuse within CB of perovskite and undergo injection which will further lead to the generation of photocurrent in the solar cell devices. While the hot electron cools down to the bottom of CB, the holes move to the top of VB through hole migration or hole transfer. And then, the interband charge relaxation leads to the electron-hole recombination.



Fig. 2 2D plots of time evolution of transient absorption spectra (ΔA) of perovskite with compact TiO₂ layers before and after UV irradiation.

As shown in Fig.2, the 2D plots of difference absorption (ΔA) as a function of wavelengths and time have a significant change after UV irradiation in region II (blue negative ΔA signals at 730-760 nm); meanwhile, there is no marked change in region I (red positive ΔA signals at 700-720 nm). The positive ΔA signals (orange color) in region I are due to the absorption of excited electronic state and the negative ΔA signals (blue color) in region II are due to the depopulation from valance bands (bleach).



Fig. 3 Temporal dynamics at 710 nm in spectral region I and 745 nm in region II of perovskite with compact TiO_2 layers before and after UV irradiation.

In order to quantitatively analyze the ΔA spectra, the dynamics over the whole spectral region (700-750 nm) were fitted by a multi-exponential function as following:

$$\Delta A(t) = A_0 + A_{fast} e^{-\frac{t}{\tau_{fast}}} + A_{slow} e^{-\frac{t}{\tau_{slow}}}$$

Figure 3 shows the typically fitting results at 710 nm in spectral region I (700-730 nm in Fig. 2) and 750 nm in region II (730-750 nm in Fig. 2) of perovskite with compact TiO₂ layer before and after UV irradiation. In region I, the fast and slow time constants are assigned to the diffusion of photoexcited electrons ($\tau_{e,dif}$) and injection to the conduction band (CB) of TiO₂ ($\tau_{e,inj}$). In the region II, the fast decaying part was assigned to the hole migration between two valance bands ($\tau_{h,tra}$). The slow rising component in region II could be assigned to the interband charge relaxation which leads to



Fig. 4 Schematic illustration of the full carrier relaxation processes in perovskite/compact TiO₂ after pumping. CB: Conduction band, VB1: Valence band 1, VB2: Valence band 2.

the electron-hole recombination (τ_{rec}) as shown in Fig.4. Finally, the amplitude of Arec in the sample with compact TiO₂ after UV irradiation is dramatically larger than that before UV irradiation[2]. The amplitude corresponding to each time constant indicates the occurrence rates of the corresponding processes. It means that more photocarriers were recombined. Because perovskite/TiO₂ heterojunction samples are exposed to UV irradiation, the light induced meta-stable trap states and accumulated hole/electron were found. The meta-stable trap states caused by oxygen vacancies are formed at the perovskite/TiO2 interface and primarily act as electron-hole recombination sites as shown in Fig. 4. Obviously, this annoying problem of UV-induced degradation in perovskite with compact TiO₂ might be solved by suppressing the process of electron-hole recombination. Recently, Chen's group demonstrated that the perovskite solar cell devices with 2D atomic sheets of titania (Ti₁₋₈O₂) exhibit excellent UV stability[3]. We will measure the carrier dynamics in this perovskite/atomic TiO₂ sample and would expect to get the result that the process of electron-hole recombination could be significantly suppressed.

3. Conclusions

We disclose the microscopic mechanism for the UV-induced degradation of perovskite/compact TiO_2 heterojunction solar cell through time-resolved fs pump-probe spectroscopy. The experiment results reveal that significantly changes in electron-hole recombination plays a vital role in the UV-induced degradation of TiO_2 -based perovskite solar cells. The results would inspire people to further improve the performance and stability in perovskite photovoltaic devices.

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