

# Carrier dynamics in planar perovskite photovoltaics with dual nanocomposite carrier transport layers studied by femtosecond spectroscopy

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## Abstract

In the present study, planar perovskite photovoltaics that incorporate dual nanocomposite carrier transport layers have been fabricated. The electron transport layer (ETL) comprising PC<sub>61</sub>BM doped with Bphen, while the hole transfer layer (HTL) comprising PEDOT:PSS doped with MoS<sub>2</sub> nanosheets were used to enhance the electron and hole mobility, respectively. The carrier dynamics of this device and the corresponding control device prepared with pristine layers were measured by femtosecond transient absorption spectroscopy. It was found that a smaller carrier recombination and injection lifetime in the double modified carrier transport layers perovskite solar cell, resulting in great enhancement (~57%) of the power conversion efficiency (PCE).

## 1. Introduction

Hybrid organic–inorganic perovskite solar cells emerge as one of the rising stars in the next-generation photovoltaics. Owing to the advantages of its panchromatic light absorption, ambipolar transport with high mobility, long carrier lifetime, and very long electron/hole diffusion lengths, the hybrid perovskite solar cells can achieve efficiency as high as 20% within a short period of time. The typical planar solar cells contain a cathode, an electron transport layer (ETL), a perovskite layer, a hole transport layer (HTL), and an anode. 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. In order to improve the carrier transport and extraction abilities, one should put great efforts into to the modification of ETL and HTL, such as suitable materials and dopants selection, and interface passivation. In this present study, we employed two nanocomposites carrier transport layers—ETL comprising the small molecule 4,7-diphenyl-1,10-phenanthroline (Bphen) doped [6,6]phenyl-C61-butyric acid methyl ester (PC<sub>61</sub>BM) and HTL comprising molybdenum disulfide (MoS<sub>2</sub>) nanosheets doped poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS)—to enhance the carrier transport from the perovskite to the electrodes. The detail structure, morphologies, and characteristics of these composite ETLs and HTLs have been systematically described and measured in [1] previously. In brief, the electron mobility when Bphen was present in the ETL was higher than that of

the neat PC<sub>61</sub>BM film. In addition, the hole mobility when MoS<sub>2</sub> was present in the ETL also increased. The much higher mobility in the devices featuring the composite ETL and HTL would presumably improve exciton dissociation and charge transfer to the cathode and anode. PC<sub>61</sub>BM blended with Bphen had a higher volume fraction, indicating that the electrons had more paths through which they could undergo transfer. In this paper, ultrafast optical pump–probe spectroscopy was used to probe the carrier dynamics and to explore the mechanism behind the enhancement of power conversion efficiency (PCE). From the transient absorption spectra measurements, it revealed that a smaller carrier recombination and a shorter injection lifetime in the perovskite solar cell doubly modified with carrier transport layers, resulting in an enhancement of the PCE.

## 2. Results and Discussion

Figure 1 presents the J–V characteristics curves of the perovskite solar cells consisting of ITO/PEDOT:PSS/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>/PC<sub>61</sub>BM and ITO/PEDOT:PSS:MoS<sub>2</sub> (0.1wt%)/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>/PC<sub>61</sub>BM:Bphen(0.5wt%), measured under standard 1 sun AM 1.5G simulated solar irradiation.

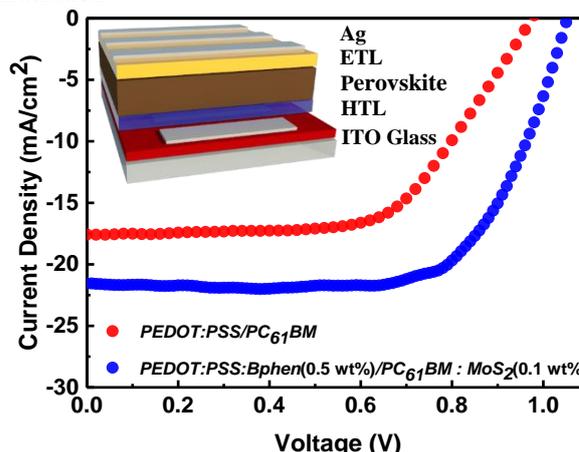


Fig. 1 Schematic representation of the structure and J–V characteristics curves of the perovskite solar cells consisting of ITO/PEDOT:PSS/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>/PC<sub>61</sub>BM and ITO/PEDOT:PSS:MoS<sub>2</sub>(0.1wt%)/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>/PC<sub>61</sub>BM:Bphen(0.5wt%), measured under standard 1 sun AM 1.5G simulated solar irradiation.

We used the ultrabroadband pump-probe spectroscopy technique to measure the time and photon energy-resolved transient absorption difference ( $\Delta A$ ) of the control sample and the sample featuring doubly modified transfer layers

sample. The samples were pumped at 400 nm to fill the perovskite conduction band, and the resulting absorption dynamics were probed with using a white light continuum from 450 to 760 nm. Fig 2 presents 3-D plots of the  $\Delta A$  spectra as functions of time and photon energy for the doubly modified transfer layer sample, which indicates three regions of  $\Delta A$  signals: one negative  $\Delta A$  signal (photoinduced absorption, PIA) at a wavelength of 540–660 nm and two positive  $\Delta A$  signals (photobleached, PB) at wavelengths of approximately 500 and 700 nm, respectively.

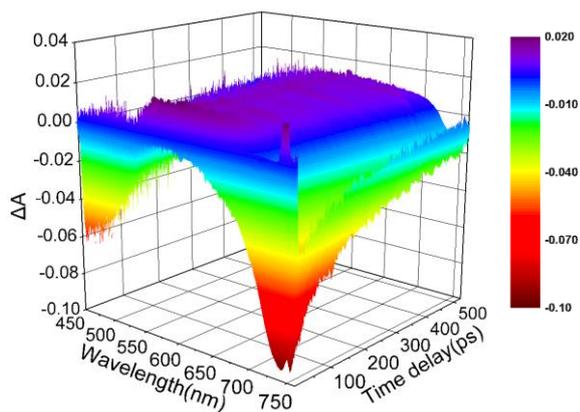


Fig. 2 3-D Plot of the ultrafast transient absorption difference ( $\Delta A$ ) on the structure: ITO/PEDOT:PSS:MoS<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>/PC<sub>61</sub>BM:Bphen.

We extracted amplitudes and lifetimes by fitting the integrated PB peak intensity to a convolution of the excitation Gaussian pulse to the following biexponential function:

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

where  $\tau_{recom}$  and  $\tau_{inject}$  correspond represent to recombination lifetimes and charge injection lifetimes, respectively;  $A_{recom}$  and  $A_{inject}$  are represent the contributions from the corresponding components, and  $A_0$  is a constant corresponding to a recombination process with having a much longer lifetime. The fast component ( $\tau_{recom}$ ) is attributed related to both charge carrier trapping at the perovskite grain boundaries or defect sites and Auger recombination[2]; the slow component ( $\tau_{inject}$ ) represents is related to carrier injection from the perovskite to the ETL or HTL. According to previous studies, we used the wavelengths of 700-720 nm for the electron dynamics and 720-745 nm for the hole dynamics[2]. In order to quantitatively analyze the  $\Delta A$  spectra, the dynamics over the whole spectral region (700-745 nm in Fig. 2) were fitted by a multi-exponential function. All of the fitted time constants corresponding to different wavelengths in two different spectral regions are shown in Fig.3(a). Figure 3(b) shows the typically fitting results at 710 nm and 730 nm of perovskite with the control sample and double modified transfer layer sample. We find both electron and hole for charge injection lifetimes are decreasing. Compared with the control sample, double modified transfer layer sample has shorter time constant in  $\tau_{recom}$  and  $\tau_{inject}$ . Additionally, we use the formula:  $A_{inject}/(A_{recom}+A_{inject})$  to represent the percentage of carrier injection in the process that carrier transfer

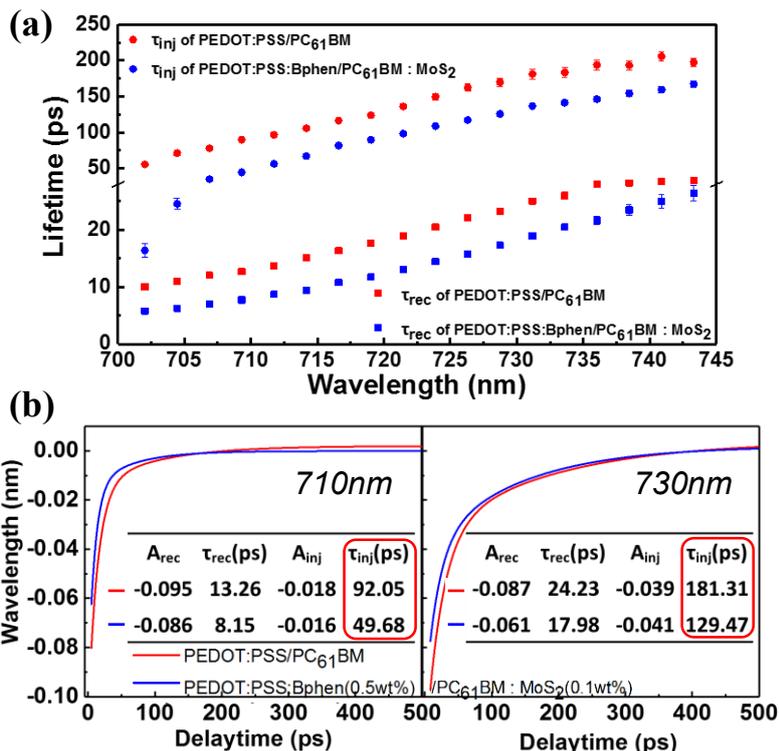


Fig. 3 (a) All of the fitted time constants corresponding to different wavelengths in two different spectral regions (b) Temporal dynamics at 710 nm and 730 nm of the structure: ITO/PEDOT:PSS/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>/PC<sub>61</sub>BM and ITO/PEDOT:PSS:MoS<sub>2</sub>(0.1wt%)/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>/PC<sub>61</sub>BM:Bphen(0.5wt%).

from perovskite boundary to electron or hole transfer layer[3]. In two regions, the percentages of electron injection and hole injection increase by 6% and 18%, respectively. The probability of recombination at the interface between the perovskite and transfer layer can decrease. Thus, there were more effective free carriers, which produced a larger value of  $J_{sc}$ , resulting in the device incorporating the doubly modified transfer layers having the highest value of PCE (16%).

### 3. Conclusions

We used quantitative pump-probe data to resolve the carrier dynamics from the perovskite to the ETL and HTL, and observed a smaller possibility of carrier recombination and a shorter injection lifetime in the perovskite solar cell doubly modified with carrier transport layers, resulting in an enhancement of the PCE.

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### References

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