

Ultrafast charge generation, high and balanced charge carrier mobilities in organo halide perovskite solar cell

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Abstract: Using terahertz and transient absorption spectroscopy, carrier dynamics in organo halide perovskite solar cell is probed. Charge generation is <100 fs, followed by 2 ps charge formation with balanced electron hole mobility of $20 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

OCIS codes: (320.0320) Ultrafast optics; (320.7130) Ultrafast processes in condensed matter, including semiconductors

1. Introduction

In the past two years, interest in organo halide perovskite based solar cells has increased dramatically. This is due to the fact that these new types of materials has reached an unprecedented overall power conversion efficiency (PCE) of 15% [1], just few months after it was introduced, and is currently on the way of reaching 20% [2]. Several groups have shown that one of the important advantages of these materials is its very long diffusion length exceeding $1 \mu\text{m}$ [3, 4]. It is, however, not clear if the long diffusion lengths are due to molecular excitons, that is, tightly bound electron-hole pairs, or due to highly mobile charge carriers. Therefore, there is an urgent need to determine the nature of its initial photophysical processes which is lacking in the present literature.

Using time resolved terahertz (THz) and optical transient absorption spectroscopy, we studied charge carrier dynamics of neat $\text{CH}_3\text{NH}_3\text{PbI}_3$, $\text{CH}_3\text{NH}_3\text{PbI}_3$ on Al_2O_3 and $\text{CH}_3\text{NH}_3\text{PbI}_3$ on TiO_2 . On the one hand, we can obtain charge generation and formation times from neat $\text{CH}_3\text{NH}_3\text{PbI}_3$. On the other hand, adding Al_2O_3 will give insight on the influence of the presence of nanoparticles (NP) to the dynamics of charge carriers. Moreover, we also studied $\text{CH}_3\text{NH}_3\text{PbI}_3$ on TiO_2 to elucidate the injection of electrons and its effect on the mobility of charge carriers.

2. Results and Discussion

Shown in Fig. 1(a) is the early time kinetics of the three samples under study measured using time resolved THz (solid line) and transient absorption (line with symbol). For neat $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Al}_2\text{O}_3$, the THz kinetics is characterized by an ultrafast (instrument response) rise followed by a 2 ps of further increase. This is in agreement with the corresponding two step rise in the transient absorption kinetics having identical timescales. From these traces, we conclude that charges are initially generated (instantaneous) which are Coulombically bound, that is, electron-hole pairs. An activation energy on the order of thermal energy, kT , is required before it dissociates to mobile charges, which in this case manifested as the 2 ps rise. In contrast, the rise of THz kinetics in $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{TiO}_2$ is just one component and is limited by our instrument. Similar ultrafast rise is observed in TiO_2 attached to either dye [5], or quantum dot [6], and assigned as electron injection. These studies and the favorable band alignment of the perovskite and metal oxide lead us to conclude that the injection is also ultrafast.

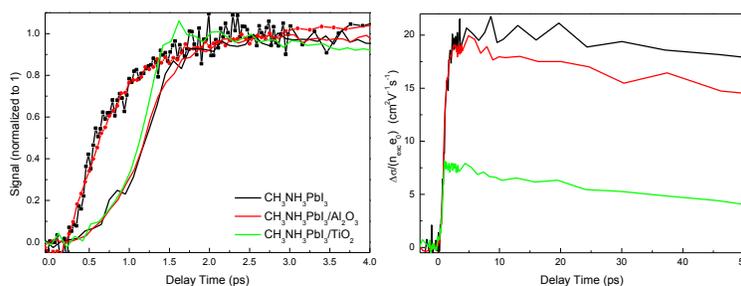


Fig. 1. (a) Transient absorption and THz kinetics of the three samples in the early timescale normalized to unity. (b) THz kinetics in the first 50 ps second showing mobility of charges normalized with $n_{exc}e$. (c) Excitation dependence of THz mobility.

Fig. 1(b) shows the THz photoconductivity kinetics normalized with excitation (n_{exc}). From the work of Hendry, et al., the intrinsic electron mobility of TiO_2 is $\ll 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [7]. Consequently, the THz mobility of $7.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{TiO}_2$ should be coming from the hole in $\text{CH}_3\text{NH}_3\text{PbI}_3$. Therefore, the electron mobility in neat $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Al}_2\text{O}_3$ should be $\sim 12.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, since the total mobility ($\mu_e + \mu_h$) is $20 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (Fig. 1(b)). The ≈ 2 ($12.5/7.5$) ratio of electron and hole mobilities in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ phase is in agreement with the recent theoretical calculations of the relative effective masses of electrons and holes [8], showing that the electron and hole mobility is almost balanced. Equally important is our finding that the mobility is very high, at least two orders higher, compared to other organic solar cell materials that we have previously measured [9,10]. Comparing the transient absorption and THz kinetics for longer timescale (not shown here), we surmised that the charge carriers maintain its very high mobility for at least 1 ns. Finally, our measurements did not resolve any difference in the charge carrier dynamics between neat $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{Al}_2\text{O}_3$.

3. Conclusion

Ultrafast generation is shown for the perovskite based solar cell materials. Due to activation (kT) energy, high mobile charges are formed within 2 ps. Electron and hole mobilities are nearly balanced explaining the very high diffusion lengths in these materials, consequently, high PCE. Furthermore, electron injection to metal oxide happens in ultrafast time scale but leads to unbalanced charge transport. This rationalizes the modest PCE when metal oxide is added to perovskite.

4. References

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