Direct Observation of Sub-picosecond Hole Injection from Lead Halide Perovskite by Differential Transient Transmission Spectroscopy

Kunie Ishioka,1,* Bobby G. Barker Jr.,2 Masatoshi Yanagida,3 Yasuhiro Shirai,3 and Kenjiro Miyano3

1Research Center for Advanced Measurement and Characterization, National Institute for Materials Science, Tsukuba, 305-0047 Japan
2Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, SC, USA
3GREEN, National Institute for Materials Science, Namiki 1-1, Tsukuba, 305-0047 Japan

(Dated: June 29, 2017)

Efficient charge separation at the interfaces between the perovskite and with the carrier transport layers is crucial for perovskite solar cells to achieve high power conversion efficiency. We systematically investigate the hole injection dynamics from MAPbI3 perovskite to three typical hole transport materials (HTMs) PEDOT:PSS, PTAA and NiOx by means of pump-probe transmission measurements. We photoexcite only near the MAPbI3/HTM interface or near the back surface, and measure the differential transient transmission between the two excitation configurations to extract the carrier dynamics directly related to the hole injection. The differential transmission signals directly monitor the hole injections to PTAA and PEDOT:PSS being complete within 1 and 2 ps, respectively, and that to NiOx exhibiting an additional slow process of 40 ps time scale. The obtained injection dynamics are discussed in comparison with the device performance of the solar cells containing the same MAPbI3/HTM interfaces.

Lead halide perovskite photovoltaic cells have been developing rapidly in the past few years, with their power conversion efficiency (PCE) now exceeding 22% [1]. The perovskites are direct semiconductors, and their photovoltaics can in principle work as a model p-i-n diode [2]. The difficulty in the controlled impurity doping in the perovskites can be circumvented by sandwiching the perovskite film between thin layers of electron- and hole-transporting materials (ETMs and HTMs) in the planar heterojunction structure [3]. These carrier transporting layers enable efficient and irreversible separation of the electrons and holes photoexcited in the perovskite, and thereby lead to the high PCE of the perovskite solar cells. Whereas various inorganic and organic materials have been explored as ETM and HTM based on their conduction band minimum (CBM) and valence band maximum (VBM) energies with respect to those of the perovskite, the actual device performance depends very weakly on the energy level offset [3, 4] but can be significantly affected by other factors such as perovskite crystalline quality and interfacial defects [5, 6].

The charge separation dynamics can in principle be monitored directly by means of transient absorption (or transmission) measurements in the visible to terahertz ranges. The time scale of the charge injection from the perovskite to the HTM layer remain controversial despite the extensive previous studies [5–14], however. The time constant of the hole injection from CH3NH3PbI3 (MAPbI3) to spiro-OMeTAD in the previous reports, for example, scattered widely from <80 fs [7] to 0.7 ps [8, 9] to 8 ps [10]. The hole injection to NiOx was reported to be complete on sub-picosecond time scale [11], whereas those to poly(tryarylamine) (PTAA), poly(3-hexylthiophene-2,5-diyI) (P3HT), and poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta [2,1-b;3,4-b’] dithiophene)-alt-4,7-(2,1,3-benzothiadiazole) (PCPDTBT) were reported to occur on sub-nanosecond time scales [12]. The wide range of the time scale over orders of magnitude appear puzzling at first glance, because the investigated HTMs have relatively similar valence band energies. The apparent inconsistency among the different studies can be contributed by the different sample preparation methods and different pump and probe light wavelengths employed, as well as by the difficulty in separating hole injection from other carrier dynamics observed in the spectroscopic signals.

In this Letter we propose a simple pump-probe method to extract the carrier injection dynamics at the interface of the perovskite and the carrier transport layer.

* ishioka.kunie@nims.go.jp

FIG. 1. (a) Energy levels of the valence band maxima (VBM) of the HTMs in comparison with the VBM and the conduction band minimum (CBM) of MAPbI3. (b) Schematics of the two different configurations of the pump-probe transmission measurements of the MAPbI3/HTM sample. Photoexcited regions inside the MAPbI3 films are designated by hatched area.

| a) | b) |
|---|---|
| MAPbI3 VBM -5.5 eV | MAPbI3 CBM -3.9 eV |
| MAPbI3 VBM -5.5 eV | MAPbI3 CBM -3.9 eV |
| PTAA PSS NiOx | 
| pump | pump |
| PMMA HTM |
| from PVK side | from HTM side |
| probe |

<arXiv:1706.09123v1 [cond-mat.mtrl-sci] 28 Jun 2017>
We measure transient transmission using excitation light whose optical absorption length is shorter than the perovskite film thickness. We take the differential transient transmission responses between excitations on the two sides of the samples, and thus directly monitors the interfacial carrier injection dynamics. We apply this method to the systematic investigation of the hole injection dynamics to the typical organic and inorganic HTMs used in the planar solar cells, PTAA, poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) and NiO$_x$, whose valence band maxima lie at slightly different energies [Fig. 1a]. We find the time constant of the hole injection and the quantity of the injected holes depend crucially on the choice of the HTM, and discuss the observed hole injection dynamics in comparison with the device performance of the solar cells containing the same interfaces.

Samples for spectroscopic measurements consist of a glass substrate, a thin layer of HTM prepared by either spin-coating (PTAA and PEDOT:PSS) or sputtering (NiO$_x$) [15, 16], and a 250-nm thick crystalline MAPbI$_3$ film [17, 18], as schematically shown in Fig. 1b. For comparison, we also prepare the sample without the HTM layer. Pump-probe transmission measurements are performed using 400-nm pump and 720-nm probe light pulses with 150-fs durations. The pump light has an absorption length considerably shorter than the perovskite film thickness ($\alpha^{-1}$=42 nm [19]) and thus provides an inhomogeneous photoexcitation only near the HTM interface or near the back surface. The probe light has an absorption length exceeding the film thickness ($\alpha^{-1}$=820 nm [19]) and monitors the carrier dynamics over the whole film thickness. By taking the difference in the transient transmissions $\Delta T$ measured in two different configurations schematically shown in Fig. 1b, we can separate the carrier dynamics directly related to the MAPbI$_3$/HTM interface from other possible effects brought by the HTM.

To discuss the hole injection dynamics in comparison with the photovoltaic device performance, we also fabricate the solar cells containing the same MAPbI$_3$/HTM interfaces and measure their current density-voltage (J-V) curves and external quantum efficiency (EQE) [20], whose results are summarized in Fig. 2 and Table I. We find that the open circuit voltage $V_{oc}$ is highest for the solar cell with PTAA, slightly lower with NiO$_x$, and lowest with PEDOT:PSS, and that the EQE is slightly higher with NiO$_x$ than with PTAA and PEDOT:PSS.

Figure 3 compares the transient transmission change $\Delta T/T$ of MAPbI$_3$ with and without HTMs. The transient signals without HTM show no systematic difference between the measurements in the two configurations: they show an instantaneous ($\lesssim$1 ps) rise after photoexcitation, followed by a monotonic decrease that can be fitted to a double exponential decay, $f(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, with time constants of $\tau_1$=0.16 and $\tau_2$=1.6 ns at pump density of 0.5 $\mu$J/cm$^2$. The instantaneous rise in $\Delta T$ can be attributed to the photoinduced bleach (PB) of the probe light by the photoexcited carriers. The faster- and slower-decaying components can be attributed to the non-geminate and Auger recombinations based on their pump density-dependences. Our observations are consistent with a previous report on 60-nm thick MAPbI$_3$ film pumped and probed at the same wavelengths [21] as well as with previous time-resolved THz spectroscopic studies [22, 23].

The presence of a thin layer of HTM modifies the transmission response of the perovskite film drastically. After the initial instantaneous rise, $\Delta T$ shows almost as rapid decrease [Fig. 3a]. Moreover, the signals measured from the HTM side ($\Delta T_{HTM}$) are substantially smaller than that from the PVK side ($\Delta T_{PVK}$) already at $\sim$1 ps after photoexcitation. Because the photoexcitation is inhomogeneous along the depth direction [Fig. 1b], the smaller $\Delta T_{HTM}$ can be attributed to the reduction in the PB as a result of the injection of holes photoexcited at the MAPbI$_3$/HTM interface. The signals from two sides eventually converge, in 100 ps for PEDOT:PSS, 250 ps for PTAA and ~2 ns for NiO$_x$ [Fig. 3b]. We attribute the convergence to the holes photoexcited on the PVK side being injected to the HTM interface after diffusing across the perovskite film, since the time scale roughly fits the expectation from theoretical simulations. On the even longer time scale, the signals from both sides de-
related with the MAPbI
∆T
the others we take the differential transient transmission
energy-relaxation, diffusion and recombination of pho-
ple arise from a variety of ultrafast phenomena including
and ∆T
PVK
HTM
3
µm
3
FIG. 3. Transient transmission changes of MAPbI
3
3
µA/cm2.

cay bi-exponentially [Fig. 3c], like we have already seen
for the perovskite without HTM. The presence of the
HTM significantly suppresses the amplitude of the fast
component A1 and slow down the decay time τ2 of the
slow component, however. At the end of our experi-
tmental time window (time delay of t=2.5 ns) ∆T with PTAA
and PEDOT:PSS becomes slightly larger than that with-
out HTM, as shown in the insert in Fig. 3c, reflecting the
larger number of electrons surviving the recombination as
a result of the deprivation of holes.

Pump-induced transmission changes ∆T can in prin-
ciple arise from a variety of ultrafast phenomena including
energy-relaxation, diffusion and recombination of pho-
toexcited electrons holes in the MAPbI3 film as well as in
the HTM layer. To extract the carrier dynamics directly
related with the MAPbI3/HTM interface and cancel out
the others we take the differential transient transmission
∆Tdiff = ∆T
PVK
− ∆T
HTM
3
NHTM(t)

FIG. 4. Differential transient transmission ∆Tdiff = ∆T
PVK
− ∆T
HTM
of MAPbI3 with different HTMs and without.

measurements; the small spike/dip at t~0 that may be
associated with the defect trapping at the MAPbI3 sur-
face or MAPbI3/glass interface. In the presence of the
PTAA layer, ∆Tdiff rises instantaneously after photoex-
citation and reaches a maximum at t=1 ps, providing the
direct evidence for the hole injection to be complete
on sub-picosecond time scale. ∆Tdiff with PEDOT:PSS
exhibits a similar time-evolution, except that it reaches
a smaller maximum at a slightly later time ( t=2 ps) af-
after an apparent two-step rise, though the contribu-
tion of the second step is small. The injection times ob-
served here are comparable with the previous report on
the sub-picosecond injection at MAPbI3/spiro-OMeTAD
[7, 8], and orders-of-magnitude faster than the nanosec-
don hole injection reported in the previous study for
the MAPbI3/PTAA photoexcited at a longer wavelength
[12]. For MAPbI3 with NiOx, the first step of the rise
is almost as fast as those with PTAA and PEDOT:PSS,
but the second step is considerably slower and contributes
larger in proportion: ∆Tdiff reaches a maximum at much
later time ( t=44 ps) as a result.

The ∆Tdiff signals decay eventually as the holes pho-
toexcited on the PVK side diffuse to the MAPbI3/HTM
interface. The time scale of the decay depends criti-
cally on the HTM, however, suggesting that the MAPbI3
films fabricated on top of the different HMT layers have
different hole diffusion constant D. Indeed, the previ-
ous studies reported different values of D, ranging from
0.01 to 4 cm2/s, for different MAPbI3 crystalline qual-
ities [10, 13, 24–26]. To quantitatively estimate the
hole diffusion for the different MAPbI3/HTM samples
we perform numerical simulations using different values
of D. Figure 5a shows examples of the hole distribu-
tions N
PVK
(z, t) and N
HTM
(z, t) for excitation on the
PVK and HTM sides in the case of D=4 cm2/s. We
then obtain the differential hole population Ndiff(t) =
N
PVK
(t) − N
HTM
(t), shown for different values of D in

for different hole diffusion constant
D.

3
FIG. 4. Differential transient transmission ∆Tdiff = ∆T
PVK
− ∆T
HTM
of MAPbI3 with different HTMs and without.
can give us hint on
the photoexcited region near the MAPbI
ancy is given in terms of the faster hole transport within
ples, however. A possible explanation for the discrep-
the experimental $\Delta T$ time scale, in rough agreement with the decay times of
$\Delta T$ is much slower than those of $\Delta T$
s reports,
and PEDOT:PSS, when calculated with the largest diffusion in bulk MAPbI
$D_{\text{diff}}$ confirms the good crystalline quality of these
perovskite films. The $N_{\text{diff}}$ part of the same
$D_{\text{diff}}$ as a function of time after photoexcitation for different values
$D$.

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*Fig. 5.* (a) Calculated hole distributions $N_{\text{PVK}}$ and $N_{\text{HTM}}$ as a function of distance $z$ from the perovskite/HTM interface for excitation on the PVK and HTM sides at different times $t$. Diffusion constant $D=4 \text{ cm}^2/\text{s}$ and recombination time $\tau=1.6$ ns are used. (c) Calculated differential number of holes $N_{\text{diff}}^S$ as a function of time after photoexcitation for different values of $D$.

In summary, we have directly monitored the hole in-
duction dynamics at the interfaces of MAPbI$_3$ with three different HTMs by measuring the differential transient transmission signals between the two sides of the sample. The hole injection to PTAA takes place at the fastest rate and the largest quantity, whereas those to PEDOT:PSS and NiO$_x$ occurs at slightly smaller rate and smaller quantity, and the solar cell exhibits slightly lower $J_{sc}$ and $V_{oc}$. The hole injection to NiO$_x$ takes an order-of-magnitude longer time than the other two HTMs, possibly because of the interfacial carrier trapping, and the solar cell shows a lower $FF$. These results suggest a tendency that not only the larger amount of the injected holes but also the faster hole injection in (sub-)picosecond time scale can lead to the better device performance, though we cannot conclude how exactly the carrier dynamics affect these device parameters.

In summary, we have directly monitored the hole in-
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