Influence of Hole Mobility on Charge Separation and Recombination Dynamics at Lead Halide Perovskite and Spiro-OMeTAD Interface

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High efficiency lead halide perovskite solar cells employ spiro-OMeTAD or PTAA as a hole transporting material. This type of hole conductor requires dopants mainly to improve hole mobility. Although such doping has improved solar cell performance, in particular open circuit photovoltage and fill factor, the mechanism of the improvement has rarely been elucidated. Here, we demonstrate influence of dopants in spiro-OMeTAD on interfacial charge separation and recombination processes for a MAPbI3 perovskite film sandwiched by an m-TiO2 film and a spiro-OMeTAD layer by employing a series of transient absorption spectroscopies. The interfacial charge recombination time was significantly retarded by the doping. We propose that the retardation of the charge recombination originates from relatively longer distance of holes from the perovskite/spiro-OMeTAD interface owing to the increased hole mobility by the doping, potentially increasing Voc of the solar cell.

Keywords: CH3NH3PbI3 perovskite, Interfacial charge recombination, OMeTAD, Charge carrier mobility

1. Introduction
Organic-inorganic hybrid perovskite solar cells (HPSCs) have recently been widely investigated as one of the most promising candidates for photovoltaic materials [1-4]. HPSCs films can be simply prepared by a low cost wet chemistry process, and possess several outstanding properties including high absorption coefficients, bandgap tunability, high charge carrier mobilities [5-8]. Perovskite photovoltaics have rapidly been developed over the last 10 years, dramatically approaching solar energy conversion efficiency of 24% [9], demonstrating remarkable competitiveness with other new generation solar cells and even with conventional silicon solar cells.

Highly efficient charge transfer reactions including high charge separation efficiency and swift charge transport are required with minimum charge recombination to show the high solar cell performance. We have previously identified underlying key parameters, i.e. photo-excitation intensity [10], device structure [11], and excitation wavelength [12], to influence and control interfacial charge transfer dynamics in CH3NH3PbI3 (MAPbI3) perovskite sandwiched by a mesoporous TiO2 (m-TiO2) film as an electron transporting materials (ETM) and a spiro-OMeTAD layer as a hole transporting material (HTM). We have also found multi-phasic electron injection reactions from MAPbI3, occurring over <1.2 to several tens of nanoseconds, considerably slower than the reported ultrafast charge transfer processes (from 200 fs to several tens of picoseconds) [13-15]. In contrast, most of holes are injected from MAPbI3 to a spiro-OMeTAD layer within the instrument response time (1.2 ns).

Following the previous reports, high efficiency HPSCs commonly employ an n-i-p structure...
utilizing spiro-OMeTAD or PTAA as a HTM. However, spiro-OMeTAD or PTAA generally suffers from low mobility (≤ 5 × 10⁻⁵ cm² V⁻¹ s⁻¹) and limited conductivity (≤ 3 × 10⁻⁷ S cm⁻¹) [16]. These HTMs thus require dopants such as lithium salt (Li-TFSI) and cobalt salt to increase the hole mobility and conductivity. Although such doping was commonly conducted and the solar cell performance was indeed improved, no clear explanation has been reported as to how effectively the increase of the HTM conductivity improves the solar cell performance. Therefore, it is crucial to clarify the difference of charge transfer mechanism in a perovskite film coated with doped HTMs and undoped HTMs, as the outcome may provide a clear idea to design high performing perovskite solar cells.

In this paper, we demonstrate influence of dopants in spiro-OMeTAD on interfacial charge separation and recombination processes for a MAPbI₃ perovskite film sandwiched by an m-TiO₂ film and a spiro-OMeTAD layer (FTO/c-TiO₂/m-TiO₂/MAPbI₃/OMeTAD), by employing a series of transient absorption spectroscopies. A model to explain the charge transfer processes will be proposed and discussed.

2. Experimental

2.1. Materials

Dehydrated PbI₂ and CH₃NH₃I (MAI) powder were purchased from Tokyo Chemical Industry, Co., Ltd. N,N-Dimethylformamide (DMF), 2-propanol and chlorobenzene were purchased from Wako Pure Chemical Industries Ltd., Japan, degassed by successive argon gas bubbling for 30 min, and dehydrated with activated molecular sieves (3A; 24 h, H₂O < 8 ppm). 2,2',7,7'-Tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) was purchased from Merck. Titanium di-isopropoxide bis(acetylatonate) was purchased from Sigma-Aldrich Co. LLC. A nanocrystalline TiO₂ paste (PST-18NR, anatase, particle diameter: ca. 20 nm) was obtained from JGC C&C.

2.2. Sample Preparation

A compact TiO₂ layer (c-TiO₂, thickness: 20 nm) was deposited on a FTO substrate by spray pyrolysis of 0.38 M titanium di-isopropoxide bis(acetylacetone) solution in 2-propanol at 450 °C [17]. A transparent mesoporous TiO₂ layer (thickness: 150 nm) was prepared on the as-prepared compact TiO₂ layer by spin coating an ethanol suspension of TiO₂ paste (TiO₂ paste:ethanol = 1:3.5 wt. ratio) at 5000 rpm for 30 s. The film was heated up to 500 °C at 15.8 °C/min, and calcined at 500 °C for 1 h in an air flow oven. The film thickness was measured by a surface profiler (KLA-Tencor P-16+).

A MAPbI₃ perovskite layer was deposited on the as-prepared FTO/c-TiO₂/m-TiO₂ inside a glove box, following the reported method [18]. A 1.0 M PbI₂ solution in dehydrated DMF was spin-coated at 70 °C. After drying at 70 °C for 1 h, the film was dipped for 40 s in a 0.06 M MAI solution in dehydrated 2-propanol, forming a perovskite structure. To remove excess amount of MAI, the film was quickly rinsed with 2-propanol and dried at 70 °C for 30 min. The obtained perovskite layer thickness is 300~500 nm. A hole-transporting layer was deposited on top of TiO₂-MAPbI₃ by spin-coating a solution of spiro-OMeTAD in dehydrated chlorobenzene (0.058 M) with and without additives containing 4-tert-butylpyridine (0.19 M), lithium bis(trifluoromethylsulphonyl)imide (0.031 M) and tris[2-(1Hpyrazol-1-yl)-4-tert-butylpyridine]cobalt(III)tris[bis(trifluoromethylsulfonyl) imide] (5.6 × 10⁻³ M).

The film was placed in a vacuum chamber with optical windows, and was kept under vacuum (~10⁻³ Torr) during steady state or transient optical measurements. For all optical experiments, the films were excited from a glass substrate side.

2.3. Characterization

Absorption spectra of perovskite deposited films were measured by a UV-Vis absorption spectrometer (Shimadzu, UV-2450). Photoluminescence spectra were collected using a PTI UV-Vis fluorometer (Photon Technology International, Inc.) with slit width of 1.0 mm (4.0 nm resolution) at room temperature. The spectra were observed using a photomultiplier detector in a wavelength range between 400 and 800 nm, and corrected for the spectral response of the grating in the emission monochromator and the detector [19].

Nanosecond transient absorption spectroscopy (ns-TAS) was employed to monitor charge transfer reactions [11]. Data were obtained by a home-built transient absorption spectrometer with a N₂ laser (LTB Lasertechnik Berlin GmbH, MNL 202-C) pumped dye laser (LTB Lasertechnik Berlin GmbH, ATM200, 700 ps pulse duration) as an excitation source. Transient absorption signal was probed by a Xe lamp (Photon Technology International) light through two monochromators (Acton, Princeton Instruments), and detected by a Si based nanosecond detection system (Unisoku Co., Ltd.,
TSP-2000SN, time resolution: 1.2 ns (FWHM), monitoring wavelengths: 400–1,100 nm) with a fast oscilloscope (Tektronix, TDS 3052C, Digital Phosphor Oscilloscope 500 MHz 5 GS/s) at 10 Hz excitation repetition rate.

Microsecond-millisecond visible to near infrared transient absorption spectroscopy (mms-TAS) was employed to monitor charge separated states and charge recombination dynamics at the perovskite interfaces. To monitor a wavelength range of 400–1,100 nm, the measurements were conducted by a home-built transient absorption spectrometer with a N₂ laser (OBB, OL-4300) pumped dye laser (OBB, OL-401, 800 ps pulse duration) as a pump source, a 100 W halogen lamp (Olympus) as a probe source, a Si photodiode-based detection system (Costronics Electronics, time resolution: ~700 ns), and a TDS-2022 Tektronix oscilloscope [20-22]. Monochromatic probe light was obtained from the halogen lamp through two monochromators (JASCO, M10). Transient data were collected with the excitation intensity of 120 μJ/cm² and a repetition rate of 2 Hz at 22 °C. To monitor a wavelength range of 900–2,500 nm, the measurements were conducted by a home-built transient absorption spectrometer with a N₂ laser (LTB Lasertechnik Berlin GmbH, MNL 202-C) pumped dye laser (LTB Lasertechnik Berlin GmbH, ATM200, 700 ps pulse duration) as a pump source, a 100 W halogen lamp (Olympus) as a probe source, InGaAs photodiode-based detection systems (Unisoku Co., Ltd., TSP-1000-NIR25, time resolution: ~150 ns), and a TDS-3012B Tektronix oscilloscope [10]. Monochromatic probe light was obtained from the halogen lamp through two monochromators (Acton, Princeton Instruments). Transient data were collected with the excitation intensity of 120 μJ/cm² and a repetition rate of 2 Hz at 22 °C. No change in steady state absorption spectra prior to and after the transient measurements was observed, when the perovskite film was fixed in the optical vacuum chamber during the laser measurements, indicating that the samples were stable during the experiments. Note that we have observed gradual degradation of the perovskite film, when the sample was left in an ambient atmosphere in air during the laser spectroscopy measurements.

3. Results
3.1. Interfacial charge separation reactions
To determine the influence of dopants in the HTM on interfacial charge transfer dynamics, we employed two different samples, (i) FTO/c-TiO₂/m-TiO₂/MAPbI₃/u-OMeTAD (undoped) and (ii) FTO/c-TiO₂/m-TiO₂/MAPbI₃/d-OMeTAD (doped). Figure 1 shows the steady-state absorption spectra for these samples. From the previous study [23], the film thickness is estimated to be 300 nm. The spectral shape with a shoulder around 750 nm is in agreement with the previous reports [10,24]. No significant difference is observed between these two spectra, indicating that the perovskite layer thickness is almost identical with negligible influence from the dopants in spiro-OMeTAD.
Figure 2 shows steady-state emission spectra for two films, glass/MAPbI₃/OMeTAD with and without dopants in spiro-OMeTAD, by comparing a perovskite layer alone on glass (glass/MAPbI₃) as a reference. Since glass is insulator, we expect to observe no charge transfer reactions after exciting the perovskite at 625 nm, and indeed we observed strong emission signal at around 775 nm. Both perovskite/OMeTAD films exhibit almost complete emission quench, suggesting that an efficient hole injection from the perovskite to the spiro-OMeTAD occurs, irrelevant to the presence or absence of the dopants. By comparing with the emission amplitude for the glass/MAPbI₃, we estimated the hole injection yield is 99.1% and 97.9% for the films with and without dopants in OMeTAD, respectively.

Figure 3. Transient absorption decays monitored at 770 nm for FTO/c-TiO₂/m-TiO₂/MAPbI₃/OMeTAD with (red dots) and without (green dots) dopants in spiro-OMeTAD excited at 625 nm with excitation intensity of 30 μJ cm⁻². The solid line shows results from the bi-exponential fitting.

We next investigated the interfacial charge transfer dynamics monitored by the TAS. Figure 3 shows the ns-TAS decays for FTO/c-TiO₂/m-TiO₂/MAPbI₃/OMeTAD with and without dopants, excited at 625 nm and monitored at 770 nm. The negative TAS signals originate from the quench of the perovskite emission, exhibiting the charge carrier (electron and hole) injection dynamics from the excited perovskite to the respective ETM and HTM layers (m-TiO₂ and spiro-OMeTAD). The TAS decays have been fitted well with a bi-exponential function, \( \Delta OD(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \), where \( \Delta OD(t) \) is the differential optical density at time \( t \), \( A_x \) is the initial amplitude of the component \( x \) (\( x = 1 \) or \( 2 \)), \( \tau \) is the exponential lifetime of the component \( x \). Both films show similar decay lifetimes with \( \tau_1 = 2.0 \) ns and \( \tau_2 = 7.2 \) ns for the doped spiro-OMeTAD film, and \( \tau_1 = 2.4 \) ns and \( \tau_2 = 8.8 \) ns for the undoped spiro-OMeTAD film, respectively. We attributed the first component to the hole injection process, and the second component to the electron injection process. By comparing these two decays, it is clear that dopants show negligible influence on the charge separation reactions at the perovskite interface.

3.2. Interfacial charge recombination reactions

We next investigated influence of the dopants in the spiro-OMeTAD on the charge separated state and interfacial charge recombination dynamics by employing mms-TAS for FTO/c-TiO₂/m-TiO₂/MAPbI₃/OMeTAD with and without the dopants. Figure 4a shows the TAS spectra for these two films monitored at 2 μs after the excitation at 625 nm with an excitation intensity of 120 μJ cm⁻². Both films indicate nearly identical TAS spectra over the wide wavelength range. The spectral amplitude has been corrected with the number of absorbed photons at the excitation wavelength for two films. The similar amplitudes of these spectra clearly indicate similar charge injection efficiency for both films, suggesting that the hole injection efficiency is not sensitive to the addition of dopants in the spiro-OMeTAD, in consistent with the above steady-state PL results and nanosecond TAS decays.

We previously assigned the broad transient absorption with the absorption peak around 1,600 nm to the absorption by the spiro-OMeTAD cation [11]. Charge recombination dynamics were observed at 1,600 nm for these two films and the results are presented in Fig. 4b. The decays were fitted with a stretched exponential function, \( \Delta OD(t) = \Delta OD_0 \exp[-(t/\tau)^\alpha] \), where \( \Delta OD(t) \) is the differential optical densities at time \( t \), \( \Delta OD_0 \) is the initial transient absorption amplitude, \( \tau \) is the characteristic stretched lifetime, and \( \alpha \) is the stretched parameter. The fitted results are summarised in Table 1. The value of the stretched parameters for these films are similar, suggesting that both charge recombination is controlled by electron trapping and detrapping process in the TiO₂ [25,26]. In contrast, the charge recombination lifetime for FTO/c-TiO₂/m-TiO₂/MAPbI₃/OMeTAD with the dopants is significantly slower (by about 30 times) than the film without the dopant. We attributed the extended lifetime of the charge recombination reaction for the
Fig. 4. (a) Transient absorption spectra for FTO/c-TiO2/m-TiO2/MAPbI3/OMeTAD without (green line) and with (red line) dopants in spiro-OMeTAD, obtained at 2 μs after 625 nm excitation with excitation intensity of 120 μJ cm⁻². (b) Transient absorption decays monitored at 1600 nm for FTO/c-TiO2/m-TiO2/MAPbI3/OMeTAD without (green dots) and with (red dots) dopants in spiro-OMeTAD. The solid line shows results from the stretched exponential fitting.

Scheme 1. Charge recombination mechanism in an m-TiO2/MAPbI3/OMeTAD film with (a) undoped spiro-OMeTAD and (b) doped spiro-OMeTAD. \(\mu_{ud}\) and \(\mu_d\) indicates the hole mobility in the undoped and doped spiro-OMeTAD, respectively. \(\tau_{ud}\) and \(\tau_d\) indicates the charge recombination lifetime in undoped and doped spiro-OMeTAD, respectively.

Table 1. Summary of the stretched exponential fitting results for charge recombination dynamics.

| Spiro-OMeTAD | Lifetime \(\tau\) / ms | Stretched parameter \(\alpha\) |
|--------------|------------------------|-----------------------------|
| Undoped      | 6.5                    | 0.32                        |
| Doped        | 220                    | 0.39                        |

doped OMeTAD film mainly to the improved hole mobility.

4. Discussion

The performance of HPSCs has been improved by including some additives such as lithium salt (Li-TFSI) and 4-tert-butylpyridine (tBP) into the spiro-OMeTAD layer [27,28]. Such doping has particularly increased an open circuit voltage (Voc) and a fill factor (FF) [27,28]. Significant increases in hole conductivity from \(10^{-8}\) to \(10^{-4}\) S cm⁻¹, and in hole mobility from \(5\times10^{-5}\) to \(2\times10^{-2}\) cm² V⁻¹ s⁻¹ were reported by doping the spiro-OMeTAD layer with LiTFSI or even oxygen [29,30]. Controlled doping to increase the conductivity of spiro-OMeTAD was demonstrated by McGehee et al.[29]. In addition, some new additives like cobalt salt (Co(III)-complex) has been employed to further increase the charge conductance, reducing the charge transport (hole) resistance of spiro-OMeTAD [14]. From these studies of increasing hole conductivity using these techniques, it is reasonable to understand improvement of the FF. We found that the increase in the hole mobility in the spiro-OMeTAD layer retards the charge recombination reactions, as shown in Fig. 4b. This retardation must originate from the relatively long distance of the holes from the perovskite/spiro-
OMeTAD interface. While the injected hole stays close to the perovskite/spiro-OMeTAD interface owing to the low hole mobility for the undoped film, most of holes can diffuse away from the perovskite/spiro-OMeTAD interface before recombining with electrons for the doped film, as shown in Scheme 1. The retarded charge recombination should also contribute to increasing the FF.

Wakamiya et al. reported the decrease of the HOMO level of spiro-OMeTAD from -5.1 to -5.2 eV by doping with Co(III)-complex (perovskite valence band edge: -5.4 eV) [23], resulting in the increased gap between the quasi-Fermi level of TiO₂ and the HOMO level of OMeTAD. Therefore, this result reasonable explains the increase of the Voc by doping the HTM. We observed indistinguishable hole injection dynamics for the films with and without the doping (Fig. 3), suggesting that the potential shift (by ~0.1 eV) by the doping shows negligible influence on the hole injection dynamics. However, the doping retards the charge recombination time. This retardation may also contribute to the increase of Voc, since such retardation in the charge recombination has been proved to increase Voc of the dye sensitised solar cells [25]. We conclude that doping spiro-OMeTAD layer can increase both Voc and FF of the solar cells based on FTO/c-TiO₂/m-TiO₂/MAPbI₃/OMeTAD, while Jsc is maintained.

5. Conclusion
We have investigated influence of dopants in spiro-OMeTAD on interfacial charge separation and recombination processes for a MAPbI₃ perovskite film sandwiched by an m-TiO₂ film and a spiro-OMeTAD layer. The hole injection processes occur within 1.2 ns, and are indistinguishable for the doped and undoped films. The charge recombination was retarded by doping spiro-OMeTAD layer, mainly attributed to the enhanced hole conductivity. These results suggest that doping spiro-OMeTAD layer can improve solar cell performance by increasing Voc and FF, while Jsc is maintained.

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