Comprehensive Interfacial Charge Transfer Study of

Metal Halide Perovskite

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

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**Declaration by candidate**

*I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.*

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List of abbreviations and symbols

PV……………….. Photovoltaic
PCE………………power conversion efficiency
TCO……………….transparent conducting oxide
OSCs………………organic solar cells
PIHSCs………….polymer/inorganic hybridized solar cells
DSSCs……………..dye-sensitized solar cells
OHPSCs……………organic-inorganic halide perovskite solar cells
D………………….donor
A………………….acceptor
ITO……………….indium-tin oxide
BHJ………………bulk heterojunction
MAPbI₃……………..methylammonium lead iodide
FET………………field effect transistors
OLED………………organic light-emitting diodes
3D………………three-dimensional
2D………………two-dimensional
PL………………photoluminescence
HTM………………hole transporting material
ETM………………electron transporting material
PSCs………………..perovskite solar cells
MAI……………….methylammonium iodide
CB………………..conduction band
VB………………..valence band
HOMO……………highest occupied molecular orbital
LUMO..................lowest unoccupied molecular orbital

\( J_{sc} \)..................short circuit current density

\( V_{oc} \)..................open circuit voltage

FF......................fill factor

AM1.5.................the solar spectrum after travelling through the atmosphere to sea level

with the sun directly overhead is referred to as "AM1". AM 1.5 means

1.5 atmosphere thicknesses, corresponds to a solar zenith angle of 78°

\( \eta \).....................the solar energy to electricity power conversion efficiency

\( P_{in} \).................the incident light power per unit area

IPCE.....................incident photon-to-current conversion efficiency

\( J_{\text{max}} \) and \( V_{\text{max}} \)...........the photocurrent density and photovoltage at the maximum obtainable

power point in \( J-V \) curves of the solar cells

EQE.....................external quantum efficiency

UV-Vis..................Ultraviolet to visible light

OD......................optical density

GSB......................ground state bleaching

SE.......................stimulated emission

PIA.....................photoinduced absorption

TAS.....................transient absorption spectroscopy

TES.....................transient emission spectroscopy

ns.......................nanosecond

\( \mu \text{s-ms} \)..............micro-millisecond

Vis-NIR.................visible to near infrared light

FWHM..................Full width at half maximum

CSLs....................charge selective layers

mp-TiO\(_2\)...............mesoporous TiO\(_2\)
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Abstract

This thesis presents a study of the charge generation, separation, and recombination processes in organic-inorganic halide perovskite solar cells (OHPSCs) performed with time-resolved experimental techniques. Perovskite solar cells based on CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) as light absorber can be solution-processed on large areas by indicating high power conversion efficiency (>22%) and thus promise to become highly cost effective source of renewable energy. Although rapid and significant improvements of the power conversion efficiency over the last four years, the fundamental working principles of OHPSCs are still not fully understood. It is the aim of this thesis to clarify the role of different performance limiting processes in perovskite solar cells and to correlate them with characters of interfacial charge transfer dynamics at the perovskite interfaces, i.e. electron transfer material (ETM) / perovskite / hole transfer material (HTM).

By combining transient absorption spectroscopy and transient emission spectroscopy in various time scale (nanosecond to millisecond) and probe light range (visible to near infrared) a comprehensive analysis of the working principles of interfacial charge transfer kinetics in MAPbI$_3$-based perovskite films could be performed. It was found that the excitation intensity severely influences the perovskite excited state lifetime and charge separation efficiency (electron and hole). The increase of excitation intensity accelerates the excited state lifetime while lowering the charge separation efficiency for both electron and hole injection yields. Moreover, the mesoscopic structure for OHPSCs has been proved to be more favorable to realize efficient electron injection compared to the planar heterojunction structure. Addition to the preferred mesoscopic structure, the best configuration for the design of perovskite device has been recommended that the perovskite absorber should be as thick as possible (>300 nm) while the mesoporous TiO$_2$ layer is supposed to be as thin as possible (<150 nm). Excitation photon energy has been found to be another key factor to influence the charge transfer dynamics. Strong excitation energy (low wavelength) can accelerate the electron injection rate while also obtaining relatively short charge recombination lifetime. The overall high performance of perovskite solar cells is highly correlated with efficient hole injection yield that is almost independent on either perovskite layer thickness or excitation energy, and also prolonged charge recombination kinetics. It is crucial to carefully consider the future application environment for perovskite solar cells based on current film structure (mp-TiO$_2$ / MAPbI$_3$ / OMeTAD), for instance, they are not suitable for high power concentrator photovoltaics (>100 sun).
Chapter 1

Introduction

1.1 Background

Nowadays, global warming induced by the emission of greenhouse gases, i.e. carbon dioxide, is undisputedly one of the most serious global environmental problems in the world. During the last decade, the worldwide concerns upon the climate change because of CO$_2$, which is briefly generated by the burning of fossil fuels such as coal, oil and gas, have been expressed from the Copenhagen summit of 2009 to the Paris Agreement of 2015. A “Carbon tax” was introduced by Australian Government in 2011 to be targeting the reduction of carbon emission.
Another chain issue accompanying with the climate change is the global energy crisis, particularly for the conventional type of energy. The employment of clean and renewable energies has turned to be more and more necessary and urgent for human beings. Solar energy is green and sustainable compared to fossil fuel, and it exhibits the feature that is more stable and controllable than nuclear energy. Comparing with other types of renewable energies such as wind energy and biomass, solar energy is nearly infinite since the daily solar energy irradiated on the earth is about 10,000 times more than the global consumed energy per day in total.\(^1\) As carriers, solar cells can realize the direct conversion from solar energy into electricity, which have been developed over the past sixty years.

1.2 Developments in solar cells

In 1950s, the research group of Daryl Chapin from U.S. Bell Laboratory prepared the first silicon substrate solar cell which obtained the photoelectric conversion efficiency of 6%.\(^2\) From then on, inorganic silicon solar cells became the hot spot of research work as the first generation of photovoltaics (PV). Until now, the solar cells based on monocrystalline silicon and polycrystalline silicon have been widely manufactured and utilized for the global PV market, whose power conversion efficiency (PCE) in lab is able to reach around 28%.\(^3\) Although the latest PCE of silicon solar cells is nearly close to the theoretical value of 30%, their shortcomings still limit the progress of large scale civilization due to sophisticated manufacturing, high energy input for mass production and inflexible property. The second-generation photovoltaics are well known as thin films solar cells, which typically consist of a transparent conducting oxide (TCO) substrate, p-i-n junction window and absorber layers,
and a back electrode. Unlike the low absorption coefficient of crystalline silicon-based solar cells due to the indirect bandgap, the applied window and absorber layers for thin films PV are all direct bandgap semiconductors with relatively higher absorption coefficient, i.e. amorphous silicon (a-Si), cadmium telluride (CdTe) and copper indium gallium selenide (CIGS), resulting in thinner thickness layers in scale of several micrometers compared to that of silicon solar cells normally thicker than 100 µm. The main advantages of thin films PV are low fabrication temperatures, relatively low energy input of production and low fabrication consumption of raw materials, leading to the largely decrease of manufacturing cost compared to crystalline silicon-based solar cells. However, thin films solar cells still suffer several problems such as low commercial efficiency of below 10% for a-Si solar cells, low stability in a hot and wet environment for CIGS solar cells, and toxicity issue for Cd-based solar cells. Consequently, the third-generation photovoltaics or called emerging solar cells have been activated and developed in the last decades, which are potentially able to overcome the Shockley–Queisser limit (see Figure 1.1) of 31% power conversion efficiency for single bandgap solar cells, mainly including organic solar cells (OSCs), polymer/inorganic hybridized solar cells (PIHSCs), dye-sensitized solar cells (DSSCs) and organic-inorganic halide perovskite solar cells (OHPSCs). The main feature of third-generation PV is to separate the functions of the light absorption and charge generation by employing an electron-transfer semiconductor as a light absorber to dissociate the charge carriers into corresponding electrodes through semiconductor-junctions, which the first- and second-generation solar cells are not able to achieve.
1.3 Emerging photovoltaics

1.3.1 Organic solar cells

Organic solar cells are devices that utilize organic semiconductors, i.e. electron-donor (D) and electron-acceptor (A) materials with matched redox energy levels, to convert the absorbed light irradiance into electrical power. An absorbed photon by organic materials results in the formation of an exciton, i.e. a pair of bound electron-hole, which is different from the formation of free carriers of electron and hole in inorganic solar cells based on p-n junctions. Initially, organic photovoltaic devices were fabricated in bilayer structure which is shown in Figure 1.2, consisting of a transparent electrode such as indium-tin oxide (ITO)
Figure 1.2 Schematic of a bilayer organic solar cell. Chemical structures of representative donor and acceptor molecules.\textsuperscript{13}

on a glass substrate, one organic light-absorbing layer as electron-donor material, one organic semiconductor layer as electron-acceptor material, and a back metal electrode such as aluminum (Al) or silver (Ag). Owing to the low dielectric constant in organic semiconductors, the binding energy is quite large in the order of 500 meV or even larger compared with that of inorganic semiconductors with just a few meV.\textsuperscript{14} Therefore, charge separation can only occur in a strong electric field or at the interface of D-A. Afterwards, charge carriers \textit{i.e.} electrons and holes, are supposed to be transferred to the corresponding electrodes through drift and diffusion processes, generating an electric current \textit{via} external circuit. Such case suggests that the morphology of the active D-A film is crucial for charge separation and transport, strongly influencing device performance. For the selection of organic components, polymers with large constituent molecules\textsuperscript{15} have attracted much attention owing to the big potentials in low-cost production by manufacturing flexible, light-weight, colorful and large-
area devices. However, the shortcomings for polymer solar cells are mainly including short lifetime and low stability with serious degradation even storage in air-free environment.\(^\text{16}\)

Due to the competition between charge transfer and charge recombination within diffusion length in organic semiconductors, the bilayer structure of organic device limits the thickness of active layer, which cannot be too thick, thus, losing sufficient light harvesting for potential high photocurrent. The blending of organic D-A materials on a nanostructured scale enables the interface to be spread throughout the device, resulting in all photo-induced charge carriers (electron and hole) are easy to find an interface for charge dissociation. This device structure with blending of organic semiconductors has become popular for the fabrication of organic PV, which is called bulk-heterojunction (BHJ) solar cells as shown in Figure 1.3.\(^\text{17}\) The most popular combination for D-A materials in organic BHJ solar cells is simply blending polymers (electron donors) with fullerene (electron acceptors) both dissolving in organic solvents.

![Figure 1.3 Schematic structure of bulk-heterojunction solar cell.\(^\text{18}\)](image)
By using diverse coating methods such as spin-coating, inkjet printing or doctor blading, a self-assembling interpenetrating network can be readily realized. Poly(3-hexylthiophene) (P3HT) is widely employed as electron-donating material in BHJ solar cells. However, due to the large bandgap of P3HT (~1.9 eV), a relatively large fraction of the solar spectrum cannot be absorbed and contribute to the photocurrent. Consequently, several low-bandgap polymers have been developed to enhance the light harvesting and potentially increase open-circuit voltage $V_{oc}$ due to their deeper HOMO (highest occupied molecular orbital) energies. To date, the most successfully developed low-bandgap polymers are poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT) and poly[4,8-bis-substituted-benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl-alt-4-substituted-thieno[3,4-b]thiophene-2,6-diyl] (PBDTTT), exhibiting a power conversion efficiency of 6.77% for the device application. Although BHJ structure allows solving the trade-off issue between exciton diffusion length and optical absorption length, organic PV still suffers several problems such as relatively low charge carrier mobility and low stability owing to the intrinsic property of organic semiconductors.

1.3.2 Organic-inorganic hybridized solar cells

Comparing with organic PV based on fully organic semiconductor materials, the bulk heterojunction solar cells with inorganic semiconductor material as electron-acceptor have been recently developed with more attractions. It has been expected that the charge mobility and device stability can be potentially improved compared to organic PV due to the metal property of inorganic semiconductors. The earliest inorganic nanoparticles as electron-
acceptor to be researched were CdSe. It possesses several merits: (i) visible light absorption range 300–650 nm, (ii) a good material compatible with polymer, (iii) easy to synthesize. In 1996, Greenham group firstly reported their work about hybrid solar cell with composite structure of MEH-PPV and CdSe nanoparticles, when weight ratio of CdSe was 90%, the cell efficiency can be 0.1%. From then on, several kinds of CdSe shape structures such as quantum dots, nanorod and tetrapod were developed widely. In 2005, Sun group prepared the hybrid solar cell with CdSe tetrapod structure whose conversion efficiency reached 2.8%. Up to 2010, Dayal group used a low bandgap material PCPDTBT as donor to improve the cell efficiency to 3.19%. To date, several various inorganic semiconductor nanocrystals or quantum dots have been successfully reported as electron-acceptor, i.e. TiO$_2$, ZnO, CdS, CdTe, PbS, CdSe and etc. Typically, BHJ structure has been commonly used for the fabrication of organic-inorganic hybridized solar cells. Similar to BHJ organic solar cells, polymer-inorganic BHJ hybrid solar cells are able to conquer the limitations of the low D-A interfacial area and inefficient charge carriers extraction. Since inorganic nanocrystals or quantum dots can be generally dissolved in organic solvents such as chloroform, toluene and chlorobenzene, which allow blending them with conjugated polymers in solution phase.

In addition, there has been another structure named ordered heterojunction (see Figure 1.4) developed successfully for polymer-inorganic hybrid solar cells. This structure is basically considered as an ideal configuration for photovoltaics, owing to the direct charge transfer pathways with managed heterojunctions. Inorganic nanocrystals or quantum dots can be grown vertically as aligned nanotubes, nanorods and nanowires onto a substrate.
Consequently, polymer molecules can be penetrated into the nanopores or even in situ synthesized by chemical oxidization method or electrochemical polymerization method. The highest reported PCE of 5.13%\textsuperscript{35} has been achieved by utilizing Sb\textsubscript{2}S\textsubscript{3} quantum dots as sensitizer and P3HT polymer as hole transporting materials, combining with mesoporous TiO\textsubscript{2} nanopores as cell configuration. However, the efficiency of organic-inorganic hybrid solar cells is still low compared to inorganic PV and the miscibility between organic and inorganic semiconductors is another issue to hinder the development of device performance.

1.3.3 Dye-sensitized solar cells

To date, dye-sensitized solar cells (DSSCs) are widely investigated as photoelectrochemical cells. It traditionally consists of transparent conducting oxide \textit{i.e.} FTO or ITO, nanocrystalline metal oxide semiconductor \textit{i.e.} TiO\textsubscript{2} or ZnO, organic colourful dye, electrolyte, and back conducting glass as counter electrode. In 1991, Gratzel’s group\textsuperscript{36} initially employed nanocrystalline TiO\textsubscript{2} in the application for DSSCs. With
respect to the working principle of DSSCs, the dye molecules absorb the sunlight under illumination and electron-hole pairs can be generated, and after charge extraction the electrons transfer to the anode electrode via TiO$_2$ nanopores while the holes transfer to the cathode electrode via electrolyte, respectively. This classic structure allows DSSCs to be very stable and obtain highest reported efficiency more than 11%.\textsuperscript{37-39} However, due to the electrolyte in liquid phase exhibiting easy volatilities and difficult encapsulations, a lot of researching works have been conducted to replace the liquid electrolyte by organic solid-state hole transporting materials, \textit{i.e.} spiro-OMeTAD.\textsuperscript{40-41} But this type of organic hole-conductor in solid state suffers fast recombination and slow charge transport, which are taken into account to be addressed for the performance improvement of DSSCs. Another research direction for DSSCs is to increase the surface area or roughness of nanocrystalline TiO$_2$ or ZnO for the enhanced adsorption of more dye molecules by synthesizing various nanostructures such as nanotubes,\textsuperscript{42-43} nanorods,\textsuperscript{44-45} or nanowires.\textsuperscript{46-47} Additionally, the interfaces between dye molecules and metal oxide with large bandgap are also crucial to determine the efficiency of DSSCs.\textsuperscript{48 ENREF_17}

1.3.4 Organic-inorganic halide perovskite solar cells

Recent researches suggest that organic-inorganic halide-based perovskites (OHPs) with methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$ or MAPbI$_3$) can be one of the most promising candidates for the development of emerging PV, which can provide a favorable combination of high PCE and low manufacturing costs.
The definition of “perovskite” originated from the crystal structure of calcium titanate (CaTiO₃), which was initially named in the honor of the Russian mineralogist Lev Perovski. For the application of optoelectronics, OHPs are a group of materials with the expression of ABX₃, where A is an organic cation (CH₃NH₃⁺ or NH₂CH₂NH₂⁺), B is a divalent cation (Pb²⁺ or Sn²⁺) and X is a monovalent halide anion (Cl⁻, Br⁻, or I⁻). Figure 1.5 shows a typical crystal structure of CH₃NH₃PbI₃ (MAPbI₃). In a unit cell of OHP structure, eight A⁺ cations such as CH₃NH₃⁺ are located at the vertices of a cubic cage, a B²⁺ such as Pb²⁺ cation is located at the center of the cube, and the latter species are octahedrally coordinated to six X⁻ species which are located at the cube’ s faces. Owing to the excellent optoelectronic properties and potential manufacturing in solution process, the OHP family of materials was initially investigated in 1990s for the new material development of field effect transistors (FET) and organic light-emitting diodes (OLED).⁴⁹-⁵⁰

The first reported use of OHP was as a dye molecule in DSSC, which achieved a 3% PCE in 2009.⁵¹ However, the OHP-based DSSCs possessed a liquid electrolyte, resulting in the
low efficiency and poor stability. In 2012, a fully OHP solid-state cell was developed with reported ~10% PCE for device fabrication.\textsuperscript{53} Hereafter, the so-called perovskite fever fully bloomed and the device performance of OHP-based solar cells has rapidly improved, and a highest reported efficiency record over 22% was obtained in 2016.\textsuperscript{54} The progress speed of OHPSCs has been incredible and unprecedented in photovoltaic history, likely attributing to several factors in relation to low-cost production, ease of solution-process, and promising optoelectronic properties.\textsuperscript{55-60} Particularly, the excellent optoelectronic properties of OHP materials as almost ideal choices have attracted extensive attentions for PV applications. The bandgap of MAPbI$_3$ is 1.55 eV that is nearly ideal for single-junction solar cells under the illumination upon the solar irradiance spectrum, and it can be adjusted in the range of 1.5-2.3 eV by changing the organic and halide ions.\textsuperscript{61-62} Since the absorption coefficient of MAPbI$_3$ is typically higher than other inorganic PV semiconductors, \textit{i.e.} Si, CdTe, and CuGa$_{x}$In$_{1-x}$S$_y$Se$_{1-y}$ (CIGS), thus the OHP absorber thickness can be decreased to thin layer with thickness of \~500 nm, leading to low material costs.\textsuperscript{63} Unlike the OPV materials, the exciton binding energy of perovskite materials is usually low in the range of \~19 meV that can realize the spontaneous exciton dissociation into free charge carriers just after light absorption.\textsuperscript{64} It is also found that the high and balanced electron and hole mobility (10 to 60 cm$^2$ V$^{-1}$ s$^{-1}$) with long charge carrier lifetime (~ 100 ns) possess long diffusion lengths (~1 µm), resulting in efficient charge transport through the 300-nm thick perovskite absorber before recombination.\textsuperscript{65}

Although OHP solar cells reveal promising potential, there are still several issues that request to be addressed prior to the possible industrialization. To date, OHPSCs have not yet
presented the high stability\textsuperscript{53, 66-67} in long term that needs to compete with the commercial silicon solar panels with 25-year lifetime. Moreover, the phenomenon of current density-voltage ($J$-$V$) hysteresis\textsuperscript{68-70} (see Figure 1.6) during voltage scanning has shown a serious concern for the production in large scale. To consider the impact factor for environment, the toxicity of Pb element in OHP materials obviously plays a negative role.

Figure 1.6 Typical current density-voltage ($J$-$V$) response with hysteresis of \textit{organic-inorganic} halide perovskite solar cell.\textsuperscript{71}
1.4 References


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63. Yin, W. J.; Shi, T.; Yan, Y. Unique properties of halide perovskites as possible origins of the superior solar cell performance. *Advanced Materials* 2014, 26 (27), 4653-4658.


Chapter 2

Literature Review

2.1 Perovskite solid-state solar cells

2.1.1 Crystal structure of perovskites

As mentioned in the previous section, the crystal structure of OHP materials (ABX₃) typically consists of a unit cell with five atoms in a cubic structure (α phase), where the cation A has twelve nearest neighbouring anions X and the cation B has six anions X as presented in Figure 2.1a. To obtain highly symmetric cubic structure, \textit{i.e.} ideal conditions, the tolerance factor $t$ should be close to 1. The tolerance factor $t$ can be expressed as a function of ionic radii of A, B and X site ions, which is shown as

$$t = \frac{(R_A+R_X)}{\sqrt{2(R_B+R_X)}}$$ (2-1)
where \( R_A, R_B, \) and \( R_X \) are the ionic radii of the corresponding ions. Distorted and low-symmetry crystal structure will be exhibited if the variation from the ideal value \( t \) is larger. Thus, to capture high-symmetry crystal structure of perovskites, \textit{i.e.} ideal tolerance factor \( t \approx 1,^1 \) the ion A must be much larger than the ion B. In general, large Pb or Sn atom is allocated at the B site, so the cation at the A site must be extremely large. At limited temperature, cubic structure\(^2\) could exist when \( t \) is in between 0.89 and 1, and smaller \( t, \text{ i.e.} t < 0.89 \), may obtain less symmetric tetragonal (\( \beta \) phase)\(^3\) or orthorhombic\(^4\) (\( \gamma \) phase) crystal structures (see Figure 2.1b and 2.1c). Besides, larger \( t, \text{i.e.} t > 1 \), could destroy the three-dimensional (3D) B-X network, replacing by a two-dimensional (2D) layer structure. Some reported DFT calculations simulated at zero temperature have shown that the orthorhombic (\( \gamma \) phase) is the most stable and the cubic (\( \alpha \) phase) is the most unstable structure, due to it is very challenging to meet the ideal condition \( t = 1.\)\(^5-7\) On the other hand, the transitions between those crystal structures usually happen in most OHP materials at limited temperature.\(^6\)

Figure 2.1 Crystal structure of (a) cubic (\( \alpha \)), (b) tetragonal (\( \beta \)) and (c) orthorhombic (\( \gamma \)) phase of MAPbX\(_3\).\(^8\)
OHP materials such as MAPbI\textsubscript{3} experiences reversible phase transition as a function of temperature.\textsuperscript{9} At low temperature of \(~100\) K, the orthorhombic (\(\gamma\)) phase could be stabilized and the phase transition between the tetragonal (\(\beta\)) phase and orthorhombic (\(\gamma\)) phase occurs at \(~160\) K. It has been reported that the tetragonal-cubic phase transition partially induces the thermal stability issue for MAPbI\textsubscript{3}-based OHPSCs.\textsuperscript{10} Additionally, some recent study concluded that the light soaking may also influence reversible structure transition in OHP materials.\textsuperscript{11}

2.1.2 Properties of MAPbX\textsubscript{3} (X = Cl, Br, I) perovskites

2.1.2.1 Optical properties

Unlike all inorganic perovskites that generally possess a large indirect energy bandgap of \(~3\) eV,\textsuperscript{12} 3D organic-inorganic halide perovskites demonstrate strong absorption in the range of visible light with a direct energy bandgap of \(~1.5\) eV particularly for MAPbI\textsubscript{3}, and large absorption coefficient that is nearly one order of magnitude higher than that of conventional dye sensitizers.\textsuperscript{13} The energy bandgap and absorption spectrum of OHP can be readily tuned by changing the ratio of halide in a hybrid perovskite (MAPbX\textsubscript{3}, X = Cl, Br, or I). Some researchers have initially probed the luminescent properties of 2D structures.\textsuperscript{14,15} It is soon found that the 3D bulk perovskites can also show broad and strong photoluminescence (PL).\textsuperscript{16} PL quantum efficiencies of up to 70\% has been reported for MAPbI\textsubscript{3-x}Cl\textsubscript{x} films prepared in solution process.\textsuperscript{17} Moreover, the PL emission wavelengths and exciton lifetimes can also be compositionally influenced by the halide in MAPbX\textsubscript{3} perovskites.\textsuperscript{18,19}
2.1.2.2 Electronic properties

Besides the excellent optical properties, the unique electronic properties also allow OHP materials to be promising in photovoltaics. An extremely long electron-hole diffusion length in order of micrometer has been announced for mixed halide (MAPbI\(_{(3-x)Cl_x}\)) and triiodide (MAPbI\(_3\)).\(^{20-21}\) Noel’s group can extensively increase the PL lifetimes by hindering non-radiative charge recombination within MAPbI\(_{(3-x)Cl_x}\) perovskite utilizing Lewis bases of thiophene and pyridine.\(^{22}\) In addition, the 3D OHP materials feature high and balanced electron and hole mobility of ~60 cm\(^2\) V\(^{-1}\) s\(^{-1}\).\(^{23}\) Therefore, efficient OHPSCs can theoretically be fabricated with no hole transporting material (HTM) owing to the ambipolar semiconducting property of perovskites.\(^{24-25}\) By assessing the deviation in efficiency of charge separation and collection across the perovskite solar cells (PSCs), Edri’s group found two significant interfaces, including one at/near the perovskite absorber/HTM, and the other at/near the perovskite absorber/electron transporting material (ETM).\(^{26}\) This work means that the PSCs function as a p-i-n device that is similar to conventional amorphous silicon based devices.

2.1.3 Device architectures

OHPSCs originally evolved from the mesoscopic structure (Figure 2.2a) in which the halide perovskite absorber exchanged the light harvesting dye.\(^{13, 27-28}\) Then, the liquid electrolyte was replaced by a solid-state hole conductor such as spiro-OMeTAD. This advanced merit stimulated big interest in the PV community and drove in researchers from the thin-film PV and OPV communities. Afterwards, planar device structures in which the
OHP semiconductor is sandwiched between ETM and HTM were made. The planar structures can be classified as either the conventional n-i-p (Figure 2.2b) or the inverted p-i-n (Figure 2.2c) structures, depending on which conducting material is encountered by the light first. Later, a mesoscopic p-i-n structure (Figure 2.2d) has also been established. Owing to the different processes, the device architecture determines the selection of charge transport (ETM and HTM) and collection (cathode and anode) materials, the corresponding material fabrication approaches, and, hence, the performance of devices.

![Schematic structures of perovskite solar cells](image)

Figure 2.2 Schematic structures of perovskite solar cells in the (a) n-i-p mesoscopic, (b) n-i-p planar, (c) p-i-n planar, and (d) p-i-n mesoscopic structures.

### 2.1.3.1 Conventional n-i-p structure

The mesoscopic n-i-p structure is the initial architecture of the perovskite photovoltaics and it is still widely employed to prepare high-performance devices. A typical structure (Figure 2.2a) is consisting of an FTO (fluorine doped tin oxide) glass as cathode, a thin
(20~50 nm thickness) compact ETM such as c-TiO₂, a 150~300 nm thick mesoporous metal oxide such as mp-TiO₂ or mp-Al₂O₃ that is penetrated with perovskites, capped with an up to 300-nm perovskite layer, a 150-200 nm thick solid-state HTM such as spiro-OMeTAD, and lastly 50-100 nm of a metal anode such as Au or Ag. In this structure, the mesoporous layer is considered to improve charge collection by reducing the charge transport distance, getting rid of direct current leakage between the two selective interfaces and enhancing light harvesting due to the scattering effect. Rather than a thick (> 500 nm) porous layer, thinning the mesoscopic layer to 150-200 nm obtains better device efficiency because of improved crystallinity in the perovskite layer. Moreover, the fraction of nanopores filling and morphology of the perovskite layer is closely in relation to the thickness of mp-TiO₂. It is found that the fraction of nanopores filling is increased and a uniform perovskite layer can homogeneously cap on top of the mesoscopic structure when the thickness of mp-TiO₂ is decreased to less than 300 nm. Complete nanopores filling along with the formation of full coverage of perovskite crystals on porous structure secures high efficiencies of charge separation and collection at the perovskite/mp-TiO₂ interface. To date, the mesoscopic n-i-p structure is still the most popular structure reporting highest PCE (22.1%) of OHPSCs.

The planar n-i-p structure (Figure 2.2b) is basically evolved from the mesoscopic structure. The initiative to employ mesoporous ETM in large area was considered to pursue high-efficiency OHP devices due to hole extraction at the HTM interfaces is extensively more efficient than electron extraction at the ETM interfaces. However, some researchers have attained high efficiencies of OHPSCs even without a mesoporous layer, by carefully controlling the formation of perovskite absorber, and the interfaces among perovskites,
charge selective layers and electrodes. The high-performance of planar n-i-p device achieved a 19.3% PCE after fine tuning the interfaces of ITO/c-TiO$_2$. The planar n-i-p perovskite device normally shows better $V_{oc}$ and $J_{sc}$ compared to the mesoscopic structure device that are prepared with same materials and method, however, the planar device tends to demonstrate more severe $J - V$ hysteresis effect owing to significantly unbalanced electron and hole transport. Therefore, the recent n-i-p perovskite devices usually contains a thin (~150 nm) mesoporous metal oxide as buffer layer infiltrated and coated with perovskites.

2.1.3.2 Inverted p-i-n structure

When the deposition sequence is reversed as the HTM is first deposited, the device is made in the p-i-n structure (Figure 2.2c). This inverted p-i-n structure device is in sequence consisting of ITO coated substrate, 50-80 nm thick p-type conducting polymer such as poly(3,4-ethylenedioxythiophene) poly(styrene-sulfonate) (PEDOT:PSS), a 300 nm thick perovskite absorber, 10~60 nm thick organic hole-blocking layer such as [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM), and a metal cathode such as Al or Ag. Actually, the planar p-i-n structure perovskite device has enabled OPV researchers to readily transfer into the field of perovskites. The recent efficiency of the planar p-i-n device has been largely improved to achieve the highest reported PCE of 18.9%, originating from a developed material preparation approach, i.e. multicycle solution coating process.

In terms of the selective contact options, recent researches have expanded from organic to inorganic materials. For instance, some metal oxide semiconductors such as NiO and ZnO/TiO$_2$ have successfully been utilized for the hole and electron selective contacts,
respectively. Furthermore, the employment of oxide HTM also triggers the fabrication of the mesoscopic p-i-n structure perovskite devices (Figure 2.2d), using NiO/mp-Al₂O₃ or c-NiO/mp-NiO as the HTM. To date, the best efficiency of the mesoscopic p-i-n device with a nanocrystalline NiO film can reach 17.3%.

2.1.4 Fabrication methods

High-quality perovskite layers usually feature good morphology and homogeneity, less purity, and appropriate crystallinity, contributing to make high-performance OHPSCs. To meet above quality requirements, high-grade compositional engineering, crystallinity controlling, and interfacial properties of perovskite layers are essential. As one critical issue, the deposition method significantly influences overall device performance even with same materials. In general, there are four popular deposition approaches to prepare OHP devices as follows: one-step solution method, two-step solution method, two-step vapor-assisted method, and dual-source vapor method.

2.1.4.1 One-step solution method

One-step solution method (Figure 2.3a) was originally used for the preparation of perovskite solid-state film and is still commonly employed for the perovskite device fabrication due to low production cost and ease of processing. Basically, organic halides such as methylammonium iodide (MAI) and lead halides (PbX₂, X = Cl, Br, or I) are mixed and dissolved in some polar solvent such as dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) to form the precursor solution. In most cases, perovskite films are deposited by spin coating the prepared precursor on substrates, besides, there are also some other solution-
based deposition methods such as spray,\textsuperscript{46} doctor-blade,\textsuperscript{47} and inkjet printing\textsuperscript{48}, with which techniques the perovskite devices show lower efficiency compared to common spin-coating method, due to so far those techniques hardly obtain well-controlled film morphology and compositional uniformity. In addition, several key factors such as precursor composition, processing temperature and environment (oxygen and humidity levels), and substrate material etc. should be carefully tuned. PCE of over 20\% has been reported using this one-step solution method.\textsuperscript{31} However, one drawback of one-step solution method is that it is difficult to achieve a homogeneous composition and uniform thickness over large areas. Solvent engineering, \textit{i.e.} the employment of several precursor solution additives and anti-solvents such as toluene, is a promising solution to address the above issue.

![Figure 2.3 Representative fabrication methods for perovskite thin films: (a) one-step solution method; (b) two-step solution method; (c) vapor-assisted solution method; (d) dual-source vapor method.\textsuperscript{28}](image)

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\textsuperscript{28}
The formation of uniform perovskite film by incorporating additives and anti-solvents is the result of decoupling the nucleation and grain growth processes.\textsuperscript{25} For precursor solutions without additives or anti-solvents, these two processes occur simultaneously. Since grain growth facilitates large-size nuclei (the free energy of volume expansion eclipses that of interface formation), the unbalanced growth rate leads to the formation of large perovskite grains with a significant number of voids between grains.\textsuperscript{33} The introduction of additives or anti-solvents retards the crystallization kinetics of perovskite formation and results in a uniform intermediate phase film during deposition. A thermal treatment provides the energy for conversion to the perovskite phase and promotes crystal growth to form pinhole-free films.\textsuperscript{28}

2.1.4.2 Two-step solution method

The two-step solution deposition approach (Figure 2.3b), or so called a sequential deposition method, was initially used by Grätzel’s group\textsuperscript{34} to produce perovskite devices with relatively high PCE > 15%. In a typical two-step solution process, a thin film is first deposited using metal halide (e.g., PbI\textsubscript{2}) precursor via spin-coating process and then the film coated substrate is dipped into the second precursor solution (e.g., MAI/isopropanol solution). Spin-coating has also been employed to drive MAI molecules into the PbI\textsubscript{2} network.\textsuperscript{49} Compared with the one-step solution method, the two-step sequential deposition approach is more suitable to attain uniform and dense perovskite layers,\textsuperscript{50} resulting in extensively being utilized to manufacture high-efficiency devices. However, one of the disadvantages of the two-step solution method is incomplete conversion of perovskites. It has been reported that the conversion speed from PbI\textsubscript{2} to MAPbI\textsubscript{3} is quite swift after the film is dipped into the
solution due to the stackable structure of heavy metal halide tends to interact with small molecules.\textsuperscript{51} As a result, a kind of dense perovskite layer is capped on the top of PbI\textsubscript{2} and retards the MAI diffusion to the underlying layer, causing incomplete perovskite conversion. This issue has been solved in some sense by recent developed techniques, \textit{i.e.} solvent engineering, by mixing PbI\textsubscript{2} precursor with some additives such as DMSO\textsuperscript{52} or H\textsubscript{2}O,\textsuperscript{53} some intermediate state of perovskites can be introduced to effectively hinder the rapid reaction among PbI\textsubscript{2} and MAI, then prevents the formation of a dense perovskite capping layer on top of PbI\textsubscript{2} layer. Accordingly, in this thesis work most of OHP films or devices have been fabricated by using the two-step solution method that will be described in detail in the forthcoming chapter.

2.1.4.3 Vapor-assisted solution method

In terms of the two-step deposition method, MAI can also be introduced through a vapor deposition technique instead of solution processing (Figure 2.3c).\textsuperscript{44, 54} This approach of deposition generally obtains well-controlled morphology and grain size through so called gas-solid crystallization, and effectively prevents film peeling that is likely to occur during liquid-solid interaction. With this vapor-assisted deposition method, it is facile to obtain full conversion of perovskite layer, however, the whole process usually requires several hours to fully complete that is one of limitations for actual application. In addition, the perovskite devices fabricated by this method have shown relatively low efficiency (~12%)\textsuperscript{55} compared to that of preparation in solution processing.

2.1.4.4 Dual-source vapor method
The dual-source vapor deposition method was initially used to prepare OHP films by Mitzi’s group in 1999. After some modification for this technique (Figure 2.3d), Snaith’s group reported the first planar heterojunction $\text{MAPbI}_\text{3-x} \text{Cl}_x$ perovskite device with a PCE of over 15%. The perovskite films prepared by dual-source vapor method are quite homogeneous and pin-hole-free, exhibiting complete surface coverage on top of charge selective contacts. Nonetheless, one big drawback of this method is that both precursor sources and products suffer low thermal stability, so that the vapor deposition generally requires exact temperature control during the vapor processing. Therefore, to date, this dual-source vapor deposition method is still limited to be used for the preparation of high-efficiency OHPSCs.

2.2 Fundamentals of perovskite solar cells

2.2.1 Working principle

Theoretically, light absorption, charge separation, charge transport, and charge collection are general photovoltaic device working processes. So as to construct them, light absorbers must be selected while investigating their optoelectronic properties. For example, a p-i-n junction is required if the light absorber is an intrinsic semiconductor, thus, a p-n junction is needed in case the light absorber features an n-type or p-type property, since n- or p-types can transport electrons or holes to the light absorber. OHP materials can be applied to either p-i-n junction or p-n junction types, because they have balanced charge transport properties. The electron and hole diffusion lengths for MAPbI$_3$ films were estimated to be $\sim$1069 nm and $\sim$1213 nm, respectively. To supplement the shorter electron diffusion length, an electron
transport layer (ETL) with a long diffusion length may be required for MAPbI$_3$. In addition, electron and hole mobilities were found to be as high as 25-60 cm$^2$ V$^{-1}$ s$^{-1}$ while the mobilities of both were nearly identical and remained high, on a microsecond time scale, along with a slow microsecond time scale for recombination.$^{58-59}$

Based on the unique property of perovskite, here, two conventional n-i-p junction structures of perovskite devices, i.e. mesoscopic (see Figure 2.4) and planar heterojunction, have been used to explain charge transfer process. After light harvesting, a pair of charge carriers, i.e. an electron and a hole, can be generated within perovskite layer. Then, the electron and the hole diffuse towards the interfaces of perovskites/charge selective layers, respectively. For mesoscopic structure device, since perovskites can penetrate in metal oxide nanopores like mp-TiO$_2$ as ETM, the electron can readily inject into mp-TiO$_2$ conduction band from perovskites while on the other hand the hole injects into HTM such as spiro-OMeTAD. For planar heterojunction structure device, the electron needs to diffuse to the
interface of compact ETM such as c-TiO$_2$ across perovskite layer, which is supposed to take more time for the electron injection compared to mesoscopic structure. After charge carriers (electron and hole) extractions to charge selective layers, the electron and the hole diffuse in ETM and HTM, respectively, towards the corresponding electrodes for charge collection. However, charge recombination process between an electron in ETM and a hole in HTM potentially occurs and competes with charge transport and collection processes, which is one of major factors to degrade overall device performance.$^{60}$ Therefore, the interfaces of perovskites/charge selective layers are critical for improving OHP device performance by realizing efficient charge separation and restrictive charge recombination.

In addition to the influence of the interface properties on device performance, the choice of the ETM and HTM is also important to achieve a high degree of charge selectivity while remaining a low surface recombination to minimize energy loss at the heterojunction interfaces. To date, a number of ETMs and HTMs have been investigated for achieving high-performance OHPSCs. Figure 2.5 shows the energy levels for several representative components of the most common OHPSCs. Nanocrystalline metal oxides are the most common ETMs. Although TiO$_2$ dominates the application in the literature, many other materials can function as either mesoporous or planar ETMs. In general, wide bandgap metal oxides, such as ZnO,$^{61-62}$ Al$_2$O$_3$,$^{63-64}$ and ZrO$_2$,$^{65}$ have been utilized to prepare devices in the
mesoscopic structure. A variety of ETMs have also been employed to make compact layer in the planar n-i-p structure, including ZnO, SnO$_2$, CdSe, and CdS. Among them, SnO$_2$ has been used to manufacture an 18% efficiency device, attributed to a good band tuning. The HTMs usually contain three categories: small molecules, organic polymer, and inorganics. Small molecules, particularly spiro-OMeTAD, are very commonly used as the HTM in high-efficiency OHPSCs. The conductive organic polymer poly(triarylamine) (PTAA) has recently attracted more attentions as a competitor to spiro-OMeTAD since it was used in the 20.2% efficiency perovskite device. Due to high materials cost and unproven long-term stability of those organic HTMs, inorganic HTMs, such as NiO, CuSCN, and CuI, are the potentials for more cost-effective and stable device performance.

Figure 2.5 Diagram presenting the energy levels, from left to right, for representative cathode, n-type (ETM), light absorber, p-type (HTM), and anode materials.
2.2.2 Dynamic competitions

Figure 2.6 shows the overview of processes and reported typical time constants of MAPbI\textsubscript{3}-based perovskite films by using nanocrystalline TiO\textsubscript{2} and spiro-OMeTAD as ETM and HTM, respectively. Following excitation, the initial separation of electrons and holes at the interface happens simultaneously after the photogeneration of the electron-hole pairs. Up to date, a wide range of electron and hole injection rate has been controversially reported in this society, i.e. the electron injection rate ($k_{e-inj}$) varies from ~1 ps to 9 ns,\textsuperscript{58, 73-74} and the hole injection rate ($k_{r-inj}$) occurs at time constants from ~1 ps to 16 ns.\textsuperscript{13, 73, 75} Recent reports have also revealed that the perovskite excited state lifetime decreases with an increase in excitation intensity,\textsuperscript{58, 76} which may influence charge separation processes. In addition, the charge recombination dynamics ($k_{cr}$) between an electron in either the TiO\textsubscript{2} conduction band (CB) or the perovskite valence band (without TiO\textsubscript{2} as ETM or back-transferring electrons from TiO\textsubscript{2} CB), and a hole at spiro-OMeTAD have been argumentatively investigated. For example, Snaith’s group reported that employing an insulator nanostructure, Al\textsubscript{2}O\textsubscript{3}, results in higher conversion efficiency compared to the TiO\textsubscript{2} film, presumably due to better charge transportation obtained by Al\textsubscript{2}O\textsubscript{3} rather than TiO\textsubscript{2} nanocrystalline.\textsuperscript{27}

Therefore, in order to maximize the power output by OHPSCs, solutions have to be done to facilitate the charge separation but hinder the charge recombination process.
2.3 Research challenges

Recent progresses in the development of newly emerged OHPSCs are really rapid. However, during this rapid growing process of OHPSCs, there are also many challenges that need to be solved to make an improved efficiency and a broad application of this type of solar cells, especially on the interfacial charge transfer mechanism and its correlation with device performance.

I. Competition between perovskite excited state and charge extraction: since the perovskite excited state lifetime has been proved to be dependent with photoexcitation intensity, thus it is crucial to deeply understand the relationship between the charge separation rate, *i.e.* electron an hole injections rates, from perovskite in excited

![Figure 2.6 Scheme of charge separation and charge recombination dynamics with reported time constants of MAPbI$_3$-based perovskite films.](image)
state into charge selective layers, *i.e.* ETM and HTM, and perovskite excited state lifetime, influenced by some key factors such as excitation intensity.

II. Thickness influencing interfacial charge transfer dynamics: OHPSCs have recently attracted more attentions on the interfacial charge transfer dynamics studies that may be controlled by several dominant parameters, such as device architectures, thickness of perovskite absorber, and thickness of mesoporous ETM, *i.e.* mp-TiO$_2$. However, there is still lack of knowledges that investigate systematically and quantitatively on parameters controlling interfacial charge transfer dynamics for perovskite films or devices. Therefore, it is urgently required to clarify how those key parameters influence the interfacial charge transfer dynamics, contributing to further improve device performance.

III. Potential level controlling charge transport kinetics: it has been found that the valence band of perovskites can vary depending on absorbed excitation energy, which may significantly influence the interfacial charge transfer dynamics between perovskites and charge selective layers. In addition, the potential levels of ETM (conduction band) and HTM (valence band) can be potentially altered by external bias application or doping with additives, respectively. Thus, it is critical to understand how the variable potential levels of perovskites, ETM and HTM control the interfacial charge transfer dynamics, supplying hints for the appropriate design of cell structure.

IV. Light intensity influencing the performance of OHPSCs: the application of OHPSCs in industry is eagerly expected to realize a revolution of next generation photovoltaics.
The incident light intensity in different areas is considered as a key factor for the device application. Hence, it is necessary to justify how the light intensity influences the performance of OHPSCs, and the correlation with the underlying characters of charge transfer dynamics.

In the next section, the research objectives will be proposed in terms of the research challenges summarized here.

2.4 Objectives of this work

This thesis aims to make contributions to the comprehensive understanding of interfacial charge transfer dynamics for organic-inorganic halide perovskite films stacked with charge selective layers (ETMs and HTMs), and the guidance of optimum perovskite cell structure for further performance improvement.

This PhD research carried out in the field of interfacial charge transfer dynamics study of MAPbI$_3$ perovskite deposited films and devices mainly include four research purposes.

1) Quantitatively analyse the charge separation efficiency with charge recombination dynamics for MAPbI$_3$ deposited films with ETM and HTM and systematically assess the photo-excitation intensity dependent electron and hole injections from MAPbI$_3$ perovskite to nanocrystalline TiO$_2$ as ETM and spiro-OMeTAD as HTM. This part of work is presented in Chapter 4.
2) Clarify the influence of several key parameters *i.e.* device architecture, thickness of perovskite absorber and nanocrystalline TiO$_2$ for mesoscopic structure, on the interfacial charge transfer dynamics for MAPbI$_3$ deposited films, supplying important recommendations for the optimum design of perovskite cell structure. This part of work is presented in Chapter 5.

3) As another key factor to understand the mechanism of perovskite cell function, the potential levels of MAPbI$_3$ perovskites and charge selective materials are supposed to make effect on the interfacial charge transfer processes. Bias application is an appropriate method to electrochemically tune the potential level of semiconductors. Thus, potential level dependent interfacial charge transfer dynamics for MAPbI$_3$ deposited films are required to be investigated. This part of work is presented in Chapter 6.

4) To correlate the interface charge transfer dynamics study with actual perovskite device performance, the light intensity dependent performance of perovskite devices is expected to be clarified. The analysis of the logarithmic light intensity dependence of the open circuit voltage indicates a slope of $1.09kT/q$, suggesting that the cell functions almost ideally with only bimolecular charge recombination and negligible leakage current. Therefore, the potential indoor application of perovskite solar cells can be expected to improve the performance by increasing the incident light intensity up to 1.2 sun. This part of work is presented in Chapter 7.
2.5 References


25. Zhou, H.; Shi, Y.; Dong, Q.; Zhang, H.; Xing, Y.; Wang, K.; Du, Y.; Ma, T. Hole-conductor-free, metal-electrode-free TiO2/CH3NH3PbI3 heterojunction solar cells based on


40. Dong, Q.; Yuan, Y.; Shao, Y.; Fang, Y.; Wang, Q.; Huang, J. Abnormal crystal growth in CH3NH3PbI3-xClx using a multi-cycle solution coating process. *Energy & Environmental Science* 2015, 8 (8), 2464-2470.


Chapter 3

Experimental Section

In the following chapter the most important experimental methods that were employed to collect data for this thesis will be discussed. First, the experimental details for evaluating the performance of OHPSCs for the determination of PCEs, *i.e.* current-voltage characteristics and external quantum efficiency, will be explained, followed by steady-state photoluminescence spectroscopy for assessing the optical properties. Transient absorption and transient emission spectroscopies are applied to study the temporal evolution of excited state populations like charge-transfer excitons or spatially separated charge carriers in OHP materials. The time delayed pulse experiment supplies insight into the interfacial charge carrier separation and recombination kinetics in OHPSCs and eventually with the help of the optimization of variable parameters. The sample preparation for all experimental techniques was maintained as closely as possible to that of solar cell devices presented in the section 3.1.2 for the sake of ensuring comparability of results between the individual experimental
methods. Further details for sample preparation are supplied in individual chapter describing the respective method (see Chapter 4-7).

3.1 Performance of MAPbI$_3$ perovskite solar cells

3.1.1 Photovoltaic characterizations

The photovoltaic performance of the fabricated MAPbI$_3$-based perovskite solar cells including the photocurrent density – photovoltage curves ($J$-$V$ curves) and the dark current potential scans are measured under AM1.5G solar simulated light (one sun condition, 100 mW/cm$^2$ at 22 ± 2 °C) from a solar simulator (HAL-320, Asahi Spectra Co. Ltd.) and using a source meter (Keithley Instruments Inc.: 2400). The simulated light power density was calibrated by a reference Si photodiode (Bunkoh-Keiki, BS-520). The $J$-$V$ curve is obtained by applying an external bias to the cell and measuring the generated photocurrent with the Source Meter under simulated solar illumination, while the dark current potential scan is performed as the same but without illumination. The voltage step and delay time of the photocurrent are 5 mV and 100 ms, respectively.

The solar energy to electricity power conversion efficiency ($\eta$) of OHPSCs is calculated by equation:

$$\eta = \frac{J_{sc}V_{oc}FF}{P_{in}} \times 100\%$$

where $J_{sc}$ is the short-circuit photocurrent density, $V_{oc}$ is the open-circuit photovoltage, $P_{in}$ is the incident light power per unit area, and $FF$ is the fill factor which is calculated by equation:
where $J_{\text{max}}$ and $V_{\text{max}}$ are the photocurrent density and photovoltage at the maximum obtainable power point respectively in $J$-$V$ curves of the solar cells.

The incident photon-to-current conversion efficiency (IPCE) as a function of wavelength is measured by using a monochromatic light source (Bunkoh-Keiki, SM-25) and a source meter (Advantest, R8240). The quantity of incident photons on the device at each wavelength is calculated by using a calibrated Si detector as a reference.

The incident photon-to-current conversion efficiency (IPCE) of OHPSCs, also known as the external quantum efficiency (EQE), is defined as:

$$IPCE = \frac{\text{Quantity of collected electrons}}{\text{Quantity of incident photons}} = \frac{h \cdot c \cdot J_{\text{sc}}}{e \cdot \lambda \cdot P_{\text{in}}}$$  \hspace{1cm} (3-3)

where $\lambda$, $e$, $h$, and $c$ are the wavelength of incident light, elementary charge, Planck constant and speed of light, respectively.

3.1.2 Device fabrication

Perovskite solar cells were fabricated by a typical two-step solution method.$^{1,2}$ A fluorine doped tin oxide (FTO, 25 mm × 25 mm) glass plate was etched with Zn powder and 2 M HCl aqueous solution. The patterned substrate was covered with a compact TiO$_2$ layer by spray pyrolysis of titanium diisopropoxide bis(acetylacetonate) in ethanol (0.05 M) at 450 °C. Subsequent spin-coating of an ethanol suspension of a TiO$_2$ paste (PST–18NR, TiO$_2$ paste:ethanol = 1:3.5 wt ratio) resulted in the deposition of ca. 200 nm-thick mesoporous
films of TiO\textsubscript{2} nanoparticles (particle diameter = ca. 20 nm). In an Ar-filled glovebox, a perovskite layer and a spiro-OMeTAD containing 4-tertbutylpyridine (0.19 M), lithium bis(trifluoromethylsulphonyl)imide (0.031 M) and tris[2-(1H-pyrazol-1-yl)-4-tert butylpyridine]cobalt(III)tris[bis(trifluoromethylsulfonyl)imide] (5.6 × 10\textsuperscript{-3} M) were coated with the method described above. For the back contact, a gold layer (80 nm) was deposited thermally on top of the device. The performance of the solar cells was measured using a 2 mm square mask in air without sealing. Devices prepared in this manner resulted in PCE of 14.7%. A sample of current density–voltage (J-V) curves of such a device is shown in Figure 3.1, indicating slight hysteresis effect for fabricated devices with the forward bias scan and reverse bias can, respectively.

3.2 Steady state UV / Vis absorption and emission spectrometer

Steady state absorption spectra of perovskite deposited films or devices were measured by a UV-Vis absorption spectrometer (Shimadzu, UV-2450).\textsuperscript{3-4} Steady state emission or also called photoluminescence spectroscopy was carried out by using a PTI UV-Vis fluorometer (Photon Technology International, Inc.)\textsuperscript{5-6} with slit widths of 1.6 mm (6.4 nm resolution) at room temperature. The spectra were observed using a photomultiplier S6 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.
3.3 Transient absorption spectroscopy

3.3.1 Introduction

Transient absorption spectroscopy is a time-resolved optical technique that allows observation of physical and chemical reactions in variable time scale since the technique of the flash photolysis was introduced by Professor Porter in the 1950’s. The principle of transient absorption spectroscopy is that a sample is illuminated with a short, intense laser pulse known as a “pump” pulse, and then corresponding changes in the optical density of the sample are monitored at a certain time delay by another short weak laser pulse known as a “probe” pulse. Therefore, this type of transient absorption spectroscopy is also named “pump-probe”. In general, there are two modes of pump-probe systems in which obtain different time resolutions. One mode is to use a continuous probe beam, and the time resolution is determined by the response time of detection electronics in the pump-probe flash photolysis system. On the other hand, another mode is to employ pulsed pump-probe spectroscopy and the time resolution is only determined by the laser pulse duration. Reaction rates are determined by comparing transient absorption decays monitored from plotting the amplitude of transmitted light against the delay time and by comparing transient spectra obtained from plotting the amplitude against probe wavelengths.

Physical and chemical reactions are observed by measuring the intensity of transmitted probe light passing through a sample after excitation, and demonstrated as differences in optical density (absorption difference or ΔOD). This ΔOD is a difference in optical density
before and after the optical excitation of the sample in transient absorption spectroscopy. Based on classic Lambert-Beer Law, $\Delta OD$ is defined by equation:

$$\Delta OD(\lambda, t) = OD_{\text{pump}}(\lambda, t) - OD_{\text{unpump}}(\lambda, t) = \log_{10}\left(\frac{I_{o,\text{unpump}}(\lambda)}{I_{o,\text{pump}}(\lambda,t)}\right) \quad (3-4)$$

where $OD_{\text{pump}}(\lambda, t)$ and $I_{o,\text{pump}}(\lambda, t)$ are the optical density and transmitted light intensity at a wavelength, respectively, after excitation at a delay time, $t$. $OD_{\text{unpump}}(\lambda)$ and $I_{o,\text{unpump}}(\lambda)$ are the optical density and transmitted light intensity without excitation of the sample.

Excited species can change the optical density of a sample by three different mechanisms: ground state bleaching (GSB), stimulated emission (SE) and photoinduced absorption (PIA). The ground state bleaching occurs whenever the ground state of a sample is partially depopulated thus the total number of sites participating in the (ground state) absorption is reduced. This results in a decrease of the optical density change in the wavelength region of the ground state absorption spectrum, which is monitored as a negative $\Delta OD$ signal. If the excited states have an emissive transition to the ground state, as is typically the case for singlet excitons, the probe pulse can induce stimulated emission from these states. This leads to a negative $\Delta OD$ signal in the spectral region of the emission spectrum of the sample. Moreover, excited species can absorb light and be excited to a higher lying state. The absorption spectra of excited species differ from the ground state absorption spectrum of a sample. Such photoinduced absorption spectra increase the optical density change of the sample in spectral regions features of the respective species and make rise to positive $\Delta OD$ signals. An exemplary transient absorption spectrum showing all of these mechanisms is presented in Figure 3.1. Transient absorption signals are generally much smaller than that of
ground state absorption, since excited states can only change the transmission of a sample by not more than a few percent even a very high initial excitation intensity is applied.

Figure 3.1 Exemplary transient absorption spectrum featuring ground state bleaching (GSB), stimulated emission (SE) and photoinduced absorption (PIA) signals.

For this thesis work, photophysical and photochemical reactions of organic-inorganic halide perovskites and perovskite deposited semiconductor films were monitored by using several transient spectrometers in various time scales. For example, a typical lifetime of MAPbI$_3$ perovskite excited state is in nanoseconds, and thus nanosecond (ns) transient absorption or emission spectroscopy can be utilized to monitor its lifetime. Furthermore, micro-millisecond (µs-ms) transient absorption spectroscopy was employed as a charge
separated state or charge recombination kinetics in ETM/perovskites/HTM films has lifetimes on μs-ms timescales.

3.3.2 Submicrosecond-millisecond Vis / NIR transient absorption spectroscopy

Submicrosecond-millisecond visible to near infrared (NIR) transient absorption spectroscopy (μs-ms-TAS) was employed to monitor charge separated states and charge recombination dynamics at the perovskite interfaces. The arrangement of the apparatus is shown in Figure 3.2. To monitor a wavelength range of 400-1,100 nm, the measurements were conducted by a home-built transient absorption spectrometer with an 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, an Si photodiode-based detection system (Costronics Electronics, probe wavelength range: 400-1,100 nm, time resolution: ~700 ns), and a TDS-2022 Tektronix oscilloscope. Monochromatic probe light was obtained from the halogen lamp through two monochromators (JASCO, M10). To monitor a wavelength range of 900-2,500 nm, the measurements were conducted by a home-built transient absorption spectrometer with an 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, probe wavelength range: 900-2,500 nm, time resolution: ~150 ns), and a TDS-3012B Tektronix oscilloscope. Monochromatic probe light was obtained from the halogen lamp through two monochromators (Acton, Princeton Instruments).
3.3.3 Nanosecond transient absorption and emission spectroscopy

Nanosecond transient absorption spectroscopy (ns-TAS)\(^8\) was employed to monitor charge separation dynamics at the perovskite interfaces. The measurements were conducted by a home-built transient absorption spectrometer with an N\(_2\) 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 an 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.

Nanosecond transient emission spectroscopy (ns-TES) was employed to monitor perovskite excited state decay dynamics. An electron or hole injection from the perovskite excited state to ETM or HTM such as nanocrystalline TiO$_2$ or spiro-OMeTAD, respectively, was also measured by following the emission quenching dynamics compared to the excited state decays observed for pristine MAPbI$_3$. Data were obtained by a home-built transient emission spectrometer with an N$_2$ laser (LTB Lasertechnik Berlin GmbH, MNL 202-C) pumped dye laser (LTB Lasertechnik Berlin GmbH, ATM200, 700 ps pulse duration) as an excitation source. The excitation laser pulse was irradiated from the glass substrate side. Emission from a perovskite layer was collected through a monochromator (Acton, Princeton Instruments), and detected by a nanosecond detection system (Unisoku Co., Ltd., TSP-2000SN, time resolution: 1.2 ns (FWHM)) with a fast oscilloscope (Tektronix, TDS 3052C, Digital Phosphor Oscilloscope 500 MHz 5 GS/s) at 10 Hz excitation repetition rate. The emission decay profile was synchronized with the excitation pulse and the detection system using a laser trigger detector.

The comparison of all utilized transient absorption/emission spectrometers based on components, monitoring time-scale, monitoring windows and time resolution, has been summarized in Table 3.1.
Table 3.1 Summary of series of transient absorption spectrometers (TAS)

<table>
<thead>
<tr>
<th>Spectrometer</th>
<th>Components</th>
<th>Monitoring Time-scale</th>
<th>Monitoring Windows</th>
<th>Time Resolution</th>
</tr>
</thead>
</table>
| **mms-Vis-TAS** | a. N₂ laser (OBB)  
 b. Dye laser (OBB)  
 c. Halogen lamp (Olympus)  
 d. Oscilloscope (Tektronix)  
 e. Si photodiode-based detection system | 700 ns-forever        | 400-1100 nm        | 700 ns          |
| **mms-NIR-TAS** | a. N₂ laser (LTB)  
 b. Dye laser (LTB)  
 c. Halogen lamp (Olympus)  
 d. Two monochromators (Acton)  
 e. Oscilloscope (Tektronix)  
 f. InGaAs photodiode-based detection system | 30 ns-forever         | 900-1600 nm        | 30 ns           |
|               |                                                  | 150 ns-forever        | 1700-2500 nm       | 150 ns          |
| **ns-Vis-TAS** | a. N₂ laser (LTB)  
 b. Dye laser (LTB)  
 c. Xe lamp (PTI)  
 d. Two monochromators (Acton)  
 e. Oscilloscope (Tektronix)  
 f. Si based nanosecond detection system (Unisoku) | 1.2 ns-forever        | 400-1100 nm        | 1.2 ns          |
3.4 References


Chapter 4 Photo-Excitation Intensity Dependent Electron and Hole Injections from Lead Iodide Perovskite to Nanocrystalline TiO₂ and Spiro-OMeTAD

Introduction

Lead halide perovskite solar cells have been recognized as a newly emerging solar cell with the potential of achieving high efficiency with low cost fabrication processes. In particular, facile solution processed cell fabrication facilitated rapid development of optimum cell structure and composition. Over the last few years, the cell efficiency has sharply increased, and now exceeds 22%. However, despite this development, fundamental operation mechanisms such as a charge separation and recombination process at perovskite interfaces have not still been explicitly understood. Based on previous intensive studies, high efficiency has been achieved by two different film structures: planar heterojunction and mesoporous structures. The latter typically consists of a nanocrystalline TiO₂ film, lead halide perovskite as a light absorber and spiro-OMeTAD hole conductor. Several studies were conducted to understand the dynamics of electron and hole injections from the perovskite. However, the reported electron injection rate varies from ~1 ps to 9 ns, and also the hole injection occurs with the time constants from ~1 ps to 16 ns. These charge separated states have not been quantitatively analysed with charge recombination dynamics. Recent reports have revealed that the perovskite excited state lifetime decreases
with an increase in excitation intensity,\textsuperscript{5} which may influence charge separation processes. Furthermore, the role of the TiO\textsubscript{2} nanocrystalline film has not explicitly been clarified.

In this chapter, the kinetic analysis of transient photoluminescence decays has been presented, resulting in an electron (to TiO\textsubscript{2}) and a hole (to OMeTAD) injection rate of 11\textpm1 ns and 1.8\textpm0.2 ns, respectively. An excitation intensity increase from 10 nJ cm\textsuperscript{-2} to 50 \textmu J cm\textsuperscript{-2} has accelerated perovskite excited state decay from 180 to 5 ns. This accelerated decay with the increased excitation intensity up to 50 \textmu J cm\textsuperscript{-2} lowers the electron and hole injection yield to 10\% and 50\%, respectively. This result suggests that under AM1.5G one sun condition (100 mW cm\textsuperscript{-2}), both electron and hole injections occur with almost 100\% efficiency. The transient absorption charge recombination study has clarified that the charge separated state lifetime was prolonged in the presence of TiO\textsubscript{2} and OMeTAD, suggesting that their presence indeed supports optimizing solar cell performance.

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References


Showcasing work from Yasuhiro Tachibana’s team at the School of Aerospace, Mechanical and Manufacturing Engineering, RMIT University, Australia.

Photo-excitation intensity dependent electron and hole injections from lead iodide perovskite to nanocrystalline TiO₂ and spiro-OMeTAD

Photo-excitation intensity dependent electron and hole injections from CH₃NH₃PbI₃ perovskite to nanocrystalline TiO₂ and spiro-OMeTAD. The electron and hole injection yield reaches 95 and 99%, respectively, under AM1.5G one sun condition (100 mW/cm²).
Photo-excitation intensity dependent electron and hole injections from lead iodide perovskite to nanocrystalline TiO$_2$ and spiro-OMeTAD†

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† Electronic supplementary information (ESI) available: Materials and experimental details; solar cell performance, SEM, XRD, photoluminescence spectra, transient emission decays and spectroelectrochemical data; and transient absorption data for N3 sensitised TiO$_2$ films. See DOI: 10.1039/c5cc06518f
‡ S.M. and M.L. contributed equally.

Photo-excitation intensity dependent electron and hole injections from CH$_3$NH$_3$PbI$_3$ perovskite to nanocrystalline TiO$_2$ and spiro-OMeTAD are presented with the electron injection yield decrease from 95% to 10% and the hole injection yield decrease from 99% to 50% by increasing the excitation intensity from 10 nJ cm$^{-2}$ to 50 μJ cm$^{-2}$.

Lead halide perovskite solar cells have been recognized as newly emerging solar cells with the potential of achieving high efficiency with low cost fabrication processes. In particular, facile solution processed cell fabrication facilitated rapid development of the optimum cell structure and composition. Over the last few years, the cell efficiency has sharply increased, and now exceeds 20%.$^5$ Based on previous intensive studies, high efficiency has been achieved by two different film structures: planar heterojunction$^7$ and mesoporous structures.$^8,9$ The latter typically consists of a nanocrystalline TiO$_2$ film, lead halide perovskite and spiro-OMeTAD. Several studies were conducted to understand the dynamics of electron and hole injections from the perovskite.$^5–11$ However, the reported electron injection rate varies from ~1 ps to 9 ns,$^5,8–12$ and the hole injection occurs at time constants from ~1 ps to 16 ns.$^6,7,9,11$ These charge separated states have not been quantitatively analysed with charge recombination dynamics. Recent reports have revealed that the perovskite excited state lifetime decreases with an increase in excitation intensity,$^5,13–15$ which may influence charge separation processes. Furthermore, the role of the TiO$_2$ film has not explicitly been clarified. Snaith et al. reported that employing an insulator nanostructure, Al$_2$O$_3$, results in higher conversion efficiency compared to the TiO$_2$ film.$^3$ Clarifying these points is extremely important to understand the charge transfer mechanisms of such films to further improve solar cell performance. Here, we employ a series of transient absorption and emission spectroscopies to quantitatively assess electron injection from the CH$_3$NH$_3$PbI$_3$ perovskite to TiO$_2$, hole injection to a spiro-OMeTAD layer, and their recombination, to clarify the role of the TiO$_2$ film.

In this study, we employ 4 different samples, (1) CH$_3$NH$_3$PbI$_3$ deposited on a TiO$_2$ nanoporous film on a glass substrate (TiO$_2$-MAPbI$_3$), (2) a spiro-OMeTAD layer deposited on top of TiO$_2$-MAPbI$_3$ (TiO$_2$-MAPbI$_3$-OMeTAD), (3) CH$_3$NH$_3$PbI$_3$ deposited on an Al$_2$O$_3$ nanoporous film on a glass substrate (Al$_2$O$_3$-MAPbI$_3$), and (4) an OMeTAD layer deposited on top of Al$_2$O$_3$-MAPbI$_3$ (Al$_2$O$_3$-MAPbI$_3$-OMeTAD). The structure of TiO$_2$-MAPbI$_3$-OMeTAD is shown in Fig. 1a,$^{16}$ and the photo of the film is shown in the inset of Fig. 1b. The film preparation details are provided in the ESI.$^†$ Note that using the identical film preparation procedure, we have achieved a solar energy conversion efficiency of 14.5% under the AM1.5G one sun condition (100 mW cm$^{-2}$), as shown in Fig. S1 (ESI†). However, for this study, to homogeneously excite CH$_3$NH$_3$PbI$_3$ inside the metal oxide nanopore, we employed a

Fig. 1 (a) Illustration of TiO$_2$-MAPbI$_3$-OMeTAD. (b) Absorption spectra of TiO$_2$-MAPbI$_3$ and Al$_2$O$_3$-MAPbI$_3$. The inset shows a photo of TiO$_2$-MAPbI$_3$ (TiO$_2$ area: 0.5 × 0.5 cm$^2$).
Fig. 2  (a) Excitation intensity dependence of transient emission decays obtained for Al2O3-MAPbI3 with 625 nm excitation. The solid line indicates a result of fitting with a rate equation (eqn (1)). The number indicates excitation intensity (unit: μJ cm⁻²). (b) Comparison of transient emission decays obtained for Al2O3-MAPbI3 and TiO2-MAPbI3 with an excitation intensity of 50 nJ cm⁻² (625 nm excitation). The solid line indicates a result of fitting with eqn (1) and eqn (S3) (ESI†), respectively. (c) Comparison of effective lifetimes obtained for Al2O3-MAPbI3 and TiO2-MAPbI3. (d) Excitation intensity dependence on electron injection yield.

2.8 μm thick TiO2 film and a 3.0 μm thick Al2O3 film. To obtain low light absorbance, lower precursor concentration (PbI2: 0.2 M) was employed to deposit CH3NH3PbI3. Fig. 1b compares absorption spectra; the absorbance difference may originate from the difference in the surface area between TiO2 and Al2O3 films. SEM images and X-ray diffraction patterns for Al2O3-MAPbI3 and TiO2-MAPbI3 are shown in Fig. S2 (ESI†). These observations suggest that the morphology and crystal structure of MAPbI3 are not influenced by the type of metal oxide nanostructure. Dependence of charge separation/recombination dynamics on the thickness of the metal oxide film and perovskite layer will be reported elsewhere.

Excitation intensity dependent transient emission decays (0.01–50 μJ cm⁻²) were observed by nanosecond transient emission spectroscopy. Fig. 2a shows emission decays for Al2O3-MAPbI3. The excitation wavelength of 625 nm was selected, not to excite PbI2 (~ 550 nm), if PbI2 remains in the perovskite layer. Since Al2O3 is an insulator, the data indicate that the perovskite excited state decays. Clearly, the excited state lifetime decreased with the increase of the excitation intensity, in agreement with the previous reports.5,11,13–15

The data were analysed by a rate equation,13,15

\[
-\frac{dn}{dt} = k_1 n + k_2 n^2
\]  

where \( n \) is the photo-excited charge carrier density, \( k_1 \) is the rate constant of trap state mediated recombination, \( k_2 \) is the rate constant of electron–hole recombination, and \( t \) is the time. Using eqn (1), the fitted results are shown as a solid line in Fig. 2a, indicating that this kinetic model agrees with the data. Similar to the previous report,13 the second order component dominates to fit the decay data obtained with an excitation intensity of >0.2 μJ cm⁻², implying that non-germinate electron–hole recombination occurs within a perovskite layer.5,13,15

We have conducted global analysis for all decays using eqn (1). The resulting first order (\( k_1 \)) and second order (\( k_2 \)) rate constants are \( 5.6 \times 10^8 \) s⁻¹ and \( 4.2 \times 10^{10} \) s⁻¹ cm⁻³, respectively. This second order rate constant is similar to those reported for flat perovskite films,13,15 suggesting that a nanoporous structure of the Al2O3 film does not influence the excited state dynamics.

Excitation intensity dependent photoluminescence decays were also observed for TiO2-MAPbI3 (Fig. S4a, ESI†). Fig. 2b shows comparison of transient emission decays obtained with 50 nJ cm⁻². The decay has clearly been accelerated for TiO2-MAPbI3 owing to the faster electron injection rate. However this acceleration is diminished when the intensity is increased. Fig. S4b (ESI†) compares transient decays obtained with 2.3 μJ cm⁻².

Since the excited state decay has first and second order components, it is not simple to evaluate the lifetime. Here, we define an effective lifetime, \( \tau_{\text{eff}} \),13 as

\[
I_{\text{PL}}(\tau_{\text{eff}}) = I_{\text{PL}}(0)/e,
\]

where \( I_{\text{PL}}(\tau_{\text{eff}}) \) is the photoluminescence intensity at time \( \tau \) after the excitation. The intensity dependent effective lifetimes are shown in Fig. 2c. An intensity increase from 0.01 to 50 μJ cm⁻² has accelerated excited state decay from 180 to 5 ns for Al2O3-MAPbI3. With low excitation intensity (<0.1 μJ cm⁻²), the difference in lifetimes between the TiO2 and Al2O3 films is nearly one order of magnitude, while the lifetimes are similar with >1 μJ cm⁻². Following these data, the electron injection rate has been estimated to be 11 ± 1 ns, using eqn (S6) and (S7) and fitted with eqn (S3) (ESI†). This injection rate is significantly slower than those reported using femtosecond transient absorption and terahertz spectroscopies (from 200 fs to several tens of picoseconds).5,6,11 In contrast, a slow (~700 ps) or no injection component was also observed.7,8,10,12 This difference may originate from the difference in excitation energy (wavelength) or multi-phasic electron injection processes, i.e. more than 3 components over fs–ns time scales, similar to dye sensitised TiO2 films.17 Recently, Douhal et al. reported an ultrafast electron injection component (200 fs) with 460 and 580 nm excitation, however no injection was observed by exciting close to the band edge at 750 nm,11 suggesting that low excitation energy (longer wavelength) may significantly lower an electron injection rate. We have also conducted excitation intensity dependent transient absorption measurements (4–120 μJ cm⁻²) to directly observe the injected electrons in TiO2 over 1000–2500 nm. However, as discussed later, no clear amplitude was observed, in agreement with the recent report.5

Intensity dependent electron injection yields were calculated using eqn (S8) (ESI†), and are shown in Fig. 2d. With an intensity of <0.1 μJ cm⁻², the yield exceeds 90%, in agreement with the quenching efficiency of the photoluminescence data (Fig. S3a, ESI†). In contrast, a gradual decrease was observed with the increase of the excitation intensity. The yield decreased up to 10% (with 50 μJ cm⁻²). Under the AM1.5G one sun condition, visible light of approximately 50 nJ cm⁻² is irradiated to a solar cell every 1 μs, suggesting that more than 90% of electron injection occurs in the solar cell based on TiO2-MAPbI3.
The hole injection process from the perovskite valence band to the OMeTAD is next assessed by comparing photoluminescence data between Al₂O₃-MAPbI₃ and Al₂O₃-MAPbI₃-OMeTAD. Fig. S3b (ESI†) shows comparison of steady state photoluminescence data, indicating significant quenching by coating an OMeTAD layer. The calculated quenching efficiency, i.e. a hole injection yield, is 96%, suggesting that a hole injection is extremely fast compared to the perovskite excited state lifetime. Excitation intensity dependent hole injection dynamics were observed by comparing photoluminescence decays, shown in Fig. 3a. For both excitation intensities of 20 nJ cm⁻² and 2.3 μJ cm⁻², clear decay acceleration was observed for Al₂O₃-MAPbI₃-OMeTAD, confirming the swift hole injection.

The intensity dependent hole injection yield was calculated using eqn (S10), and is shown in Fig. 3b. With relatively low intensity (<100 nJ cm⁻²), the yield reaches nearly 100%. The intensity increase decreases a yield up to 50% (with 50 μJ cm⁻²). Following these data, the hole injection rate is estimated to be 1.8 ± 0.2 ns. This value almost agrees with the reported values.¹⁴ Note that this hole injection rate probably indicates the slowest time, since the time resolution of our spectroscopy is limited to 1.2 ns (FWHM). Similar to the electron injection, a wide range of rate constants (200 fs–700 ps) for the hole injection were reported.⁶,⁷,¹¹,¹⁴ The variation may originate from the multi-phasic dynamics or difference in sample preparation influencing energy levels of OMeTAD to the MAPbI₃ valence band edge.

We now turn to the assessment of the charge separated state and recombination dynamics observed by Vis-NIR transient absorption (TA) spectroscopies. TA spectra at 2 μs after 625 nm excitation for TiO₂-MAPbI₃ and Al₂O₃-MAPbI₃ are shown in Fig. 4a. The residual emission from the excited state was observed at 700–900 nm. If the electron injection occurs for TiO₂-MAPbI₃, we could expect to observe a positive amplitude at 1000–2500 nm, as shown in Fig. S6 (ESI†). The TA spectrum of the N3 sensitised TiO₂ film (Fig. S5b, ESI†) indicates a positive amplitude of 0.1 mΔOD at 2500 nm (excitation intensity: 120 μJ cm⁻²), assigned to TA by electrons in TiO₂.¹⁸ Using this value and the intensity dependent electron injection yield (Fig. 2d), the estimated amplitude of absorption by electron for TiO₂-MAPbI₃ is approximately 0.5–5 μΔOD at 2500 nm over 4–120 μJ cm⁻² excitation. Such a small amplitude can be buried in noise in our spectrometer.

TA spectra were also observed for TiO₂-MAPbI₃-OMeTAD and Al₂O₃-MAPbI₃-OMeTAD (Fig. 4b). The amplitudes with a peak at around 1600 nm were observed, and are similar to the OMeTAD oxidized state shown in Fig. S6 (ESI†). Therefore, these spectra must indicate charge separated state with a hole at the OMeTAD. The larger amplitude was observed for TiO₂-MAPbI₃-OMeTAD. Since the data were normalized with the film absorbance at 625 nm, i.e. the number of absorbed photons is identical for TiO₂-MAPbI₃-OMeTAD and Al₂O₃-MAPbI₃-OMeTAD, the difference of the amplitudes must originate from the electron injection from the perovskite into TiO₂ (11 ns), following the hole transfer from the perovskite to the OMeTAD (1.8 ns). The charge separated state spectrum with an electron in TiO₂ and a hole at the OMeTAD was created spectroelectrochemically (Fig. S6 and Fig. 4b, ESI†), and is similar to the TA spectrum obtained for TiO₂-MAPbI₃-OMeTAD. Using this spectrum and the charge separated state spectrum of a N3 sensitised TiO₂ film (Fig. S5b, ESI†), the estimated electron injection yield is approximately 25%. Comparison of this yield with the intensity dependent electron injection yield shown in Fig. 2d (less than 10% with 120 μJ cm⁻²) suggests that the increase of the electron injection yield must be assisted by the faster hole injection from the perovskite to the OMeTAD.

Charge recombination dynamics were measured for TiO₂-MAPbI₃-OMeTAD and Al₂O₃-MAPbI₃-OMeTAD. The OMeTAD oxidized state decays monitored at 1600 nm are shown in Fig. 4c. In both cases, the reactions clearly occur over a wide range of time scales from <1 μs to 500 ns. Compared to the charge recombination dynamics observed for the N3 sensitised TiO₂ film, shown in Fig. S5c (ESI†), the charge recombination between an electron...
in the TiO$_2$ conduction band and a hole at the OMeTAD is approximately 20 times slower with an effective lifetime of 5.7 ms (stretched parameter $x$: 0.42). This is probably owing to the longer distance between the electron and the hole to recombine over the perovskite layer thickness.

The recombination of the hole at the OMeTAD with the electron in the perovskite conduction band appears to occur in even faster time scale ($<150$ ns, the instrument response). If the hole injection yields are identical for TiO$_2$-MAPbI$_3$-OMeTAD and Al$_2$O$_3$-MAPbI$_3$-OMeTAD, about half of holes at the OMeTAD recombine within 150 ns, significantly faster than the recombination between an electron in the TiO$_2$ conduction band and a hole at the OMeTAD. This fast charge recombination supports relatively small TA amplitudes obtained for Al$_2$O$_3$-MAPbI$_3$-OMeTAD, shown in Fig. 4b.

Scheme 1 shows an energy level diagram of TiO$_2$-perovskite/spiro-OMeTAD film. The energy level of each material was obtained from the previous reports.$^{3,4,10}$ The perovskite excited state lifetime (5–180 ns) depends upon the excitation intensity. In conclusion, we have identified that accelerated excited state dynamics is required to assess electron injection dynamics. A similar electron injection rate (10 ns) was recently observed for the CH$_3$NH$_2$PbBr$_3$ perovskite deposited TiO$_2$ film.$^{21}$ Therefore, the similar electron and hole injection mechanisms can be expected for other organometal halide deposited TiO$_2$ films with OMeTAD.

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Notes and references

Electronic Supplementary Information

Photo-excitation intensity dependent electron and hole injections from lead iodide perovskite to nanocrystalline TiO₂ and spiro-OMeTAD

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1. Materials

Dehydrated PbI$_2$ was obtained by our simple purification method or distillation,$^1$ and is now commercially available from Tokyo Chemical Industry, CO., LTD. (TCI). Dehydrated form of PbI$_2$ was essential to prepare CH$_3$NH$_3$PbI$_3$ perovskite layer by two-step solution method.$^{1-5}$ CH$_3$NH$_3$I was provided from TCI. The solvents $N,N$-dimethylformamide (DMF, super dehydrated, Wako Pure Chemical Industries Ltd., Japan), 2-propanol (super dehydrated, Wako Pure Chemical Industries Ltd., Japan), and chlorobenzene (special grade, Wako Pure Chemical Industries Ltd., Japan) were degassed by consecutive argon gas bubbling for 30 min, and dehydration with activated molecular sieves (3A; 24 h, H$_2$O < 8 ppm). 2,2’,7,7’-Tetrakis($N,N$-di-$p$-methoxyphenylamine)-9,9’-spirobifluorene (spiro-OMeTAD) was purchased from Merck. Tris[2-(1H-pyrazol-1-yl)-4-tert-butylpyridine]cobalt(III) tris[bis(trifluoromethylsulfonyl)imide] was prepared following the reported method.$^6$ A nanocrystalline TiO$_2$ (anatase structure) paste was provided from JGC C&C. Al$_2$O$_3$ powder (Aeroxide Alu C, particle diameter: approximately 13 nm) was provided from Evonik Degussa GmbH. Deuterated acetonitrile (acetonitrile-d$_3$, 99.5 % pure) was purchased from Sigma-Aldrich Co. LLC., and used without further purification.
2. Experimental

2.1 Preparation of perovskite deposited nanocrystalline films with spiro-OMeTAD

Transparent TiO$_2$ nanocrystalline films (thickness: 2.8 $\mu$m) were prepared by the screen printing method with the TiO$_2$ paste on a glass slide. The film, after printing, was leveled for 15 min, heated up to 500 °C at 15.8 °C/min, and calcined at 500 °C for 1 h in an air flow oven. Al$_2$O$_3$ nanocrystalline films (thickness: 3.0 $\mu$m) were prepared by the same screen printer with the different printing mask, using a home-made Al$_2$O$_3$ paste, following the previously reported method.$^{7, 8}$ The printed Al$_2$O$_3$ films were calcined at 500 °C for 1 h in an air flow oven. The thickness of these metal oxide nanoporous films was measured by a surface profiler (KLA-Tencor P-16+). A CH$_3$NH$_3$PbI$_3$ perovskite layer was deposited on the nanocrystalline TiO$_2$ (TiO$_2$-MAPbI$_3$) and Al$_2$O$_3$ (Al$_2$O$_3$-MAPbI$_3$) film inside a glove box, similar to the reported method.$^1$ In order to excite the perovskite layer homogeneously for the laser experiments, a thick metal oxide nanocrystalline film and a thin perovskite layer in the film was prepared. Low concentrated solution of PbI$_2$ (0.2 M) in dehydrated (H$_2$O < 8ppm) N,N-dimethylformamide (DMF) was introduced to coat on the surface of the TiO$_2$ or Al$_2$O$_3$ nanopore during the spin-coating at 70 °C. After drying at 70 °C for 1 h, the film was dipped for 20 s in a 0.06 M solution of CH$_3$NH$_3$I in 2-propanol (H$_2$O < 8ppm), forming into a perovskite layer. The films were quickly rinsed with 2-propanol and dried at 70 °C for 30 min. For some films, the hole-transporting layer was deposited on top of TiO$_2$-MAPbI$_3$ and Al$_2$O$_3$-MAPbI$_3$ by spin-coating a solution of spiro-OMeTAD in chlorobenzene (0.058 M, H$_2$O < 8ppm). The resultant films were denoted as TiO$_2$-MAPbI$_3$-OMeTAD and Al$_2$O$_3$-MAPbI$_3$-OMeTAD, respectively. The film was fixed 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.

### 2.2 Fabrication of solar cells

Perovskite solar cells were fabricated by the reported method. A fluorine doped tin oxide (FTO, 25 mm × 25 mm) glass plate was etched with Zn powder and 2 M HCl aqueous solution. The patterned substrate was covered with a compact TiO$_2$ layer by spray pyrolysis of titanium diisopropoxide bis(acetylacetonate) in ethanol (0.05 M) at 450 °C. Subsequent spin-coating of an ethanol suspension of a TiO$_2$ paste (PST–18NR, TiO$_2$ paste:ethanol = 1:3.5 wt ratio) resulted in the deposition of ca. 200 nm-thick mesoporous films of TiO$_2$ nanoparticles (particle diameter = ca. 20 nm). In an Ar-filled glovebox, a perovskite layer and a spiro-OMeTAD containing 4-tert-butylpyridine (0.19 M), lithium bis(trifluoromethylsulphonyl)imide (0.031 M) and tris[2-(1H-pyrazol-1-yl)-4-tert butylpyridine]cobalt(III)tris[bis(trifluoromethylsulfonyl)imide] (5.6 × 10$^{-3}$ M) were coated with the method described above. For the back contact, a gold layer (80 nm) was deposited thermally on top of the device. The performance of the solar cells was measured using a 2 mm square mask in air without sealing.

### 2.3 Optical measurements

#### 2.3.1 Steady state absorption and photoluminescence measurements

Absorption spectra of perovskite deposited films were measured by a UV-Vis absorption spectrometer (Shimadzu, UV-2450). Photoluminescence spectra of the film were collected using a PTI UV-Vis fluorometer (Photon Technology International, Inc.) with slit widths of 1.6 mm (6.4 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.

2.3.2 Nanosecond transient emission measurements

Nanosecond transient emission spectroscopy (ns-TES) was employed to monitor perovskite excited state decay dynamics. An electron or hole injection from the perovskite excited state to the TiO$_2$ or to spiro-OMeTAD was also measured by following the emission quenching dynamics compared to the excited state decays observed for Al$_2$O$_3$-MAPbI$_3$. Data were obtained by a home-built transient emission spectrometer with a N$_2$ laser (LTB Lasertechnik Berlin GmbH, MNL 202-C) pumped dye laser (LTB Lasertechnik Berlin GmbH, ATM200, 700 ps pulse duration) as an excitation source. The excitation wavelength was 625 nm, not to excite TiO$_2$ (by ~400 nm)$^9$ and PbI$_2$ (by ~550 nm),$^{10}$ if PbI$_2$ remains in the perovskite layer. The excitation laser pulse was irradiated from the substrate (the metal oxide film) side. Emission from a perovskite layer was collected through a monochromator (Acton, Princeton Instruments), and detected by a nanosecond detection system (Unisoku Co., Ltd., TSP-2000SN, time resolution: 1.2 ns (FWHM)) with a fast oscilloscope (Tektronix, TDS 3052C, Digital Phosphor Oscilloscope 500 MHz 5 GS/s) at 10 Hz excitation repetition rate. The emission decay profile was synchronized with the excitation pulse and the detection system using a laser trigger detector.

2.3.3 Microsecond-millisecond visible transient absorption measurements

Microsecond-millisecond visible transient absorption spectroscopy (mms-Vis-TAS) was employed to monitor charge separated states at the perovskite interfaces. The measurements were conducted by a home-built transient absorption spectrometer with a N$_2$ 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, probe wavelength range: 400~1,100 nm, time resolution: ~700 ns), and a TDS-2022 Tektronix oscilloscope. Monochromatic probe light was obtained from the halogen lamp through two monochromators (JASCO, M10). Transient data were collected with 625 nm excitation with a repetition rate of 2 Hz at 22 °C. The pulse excitation intensity was adjusted to 120 μJ/cm² to correlate with a control data using the TiO₂ film (thickness: 2.8 μm) sensitized by cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II), N3 (Solaronix). 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.

2.3.4 Microsecond-millisecond near infrared transient absorption measurements

Microsecond-millisecond near infrared transient absorption spectroscopy (mms-NIR-TAS) was employed to monitor charge separated states and charge recombination dynamics at the perovskite interfaces. 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, probe wavelength range: 900~2,500 nm, time resolution: ~150 ns), and a TDS-3012B Tektronix oscilloscope. Monochromatic probe light was obtained from the halogen lamp through two monochromators (Acton, Princeton Instruments). Transient data were collected with 625 nm excitation with a repetition rate of 1 or 2 Hz at 22 °C. The
excitation intensity was adjusted to 120 $\mu$J/cm$^2$ to correlate with a control data using the N3 sensitised TiO$_2$ film (thickness: 2.8 $\mu$m), as discussed above. The data were normalized considering the absorbance at 625 nm excitation, i.e. the number of absorbed photons is identical for both TiO$_2$ and Al$_2$O$_3$ films. The perovskite film was maintained in vacuum during the laser experiments, as mentioned above.

2.3.5 Analysis of transient emission data and charge injection yield

The increase of the excitation intensity results in acceleration of the photoluminescence decay dynamics. These decay kinetics, comparing between Al$_2$O$_3$-MAPbI$_3$ and TiO$_2$-MAPbI$_3$ and between Al$_2$O$_3$-MAPbI$_3$ and Al$_2$O$_3$-MAPbI$_3$-OMeTAD, were analyzed by a rate equation including a first order recombination via carrier trap states, second order non geminate free carrier (electron and hole) recombination and charge transfer processes, as shown in Equation S1.

$$-\frac{dn}{dt} = k_1 n + k_2 n^2 + k_{e\text{-}inj} n + k_{h\text{-}inj} n$$

(S1)

where $n$ is the photo-excited charge carrier density, $k_1$ is the rate constant of trap state mediated recombination, $k_2$ is the rate constant of electron-hole recombination, $k_{e\text{-}inj}$ is the injection rate of the electron from perovskite to TiO$_2$ conduction bands, $k_{h\text{-}inj}$ is the injection rate of the hole from a perovskite valence band to spiro-OMeTAD, and $t$ is the time. Here, we do not include three body Auger recombination, since the excitation intensity is relatively small.$^{11}$

For analysis of the perovskite excited state, i.e. data for Al$_2$O$_3$-MAPbI$_3$, Equation S1 is simplified to$^{2,11}$
\[ -\frac{dn}{dt} = k_1n + k_2n^2 \quad (S2) \]

For analysis of the electron injection dynamics, i.e. data for TiO₂-MAPbI₃, Equation S1 is simplified to,

\[ -\frac{dn}{dt} = k_1n + k_2n^2 + k_{e-inj}n \quad (S3) \]

For analysis of the hole injection dynamics, i.e. data for Al₂O₃-MAPbI₃-OMeTAD, Equation S1 is simplified to,

\[ -\frac{dn}{dt} = k_1n + k_2n^2 + k_{h-inj}n \quad (S4) \]

Charge injection yields were estimated by comparing lifetimes of the observed photoluminescence decays. Since the excited state decay has two components, i.e. first and second order components, it is not simple to evaluate the lifetime. Here, we define an effective lifetime, \( \tau_{1/e} \),

\[ I_{PL}(\tau_{1/e}) = I_{PL}(0)/e \quad (S5) \]
where $I_{PL}(\tau_{1/\epsilon})$ is the intensity of photoluminescence at time $\tau$ after the excitation. Charge injection yields were evaluated using the following equations, and the electron and hole injection yield was estimated using Equation S8 and S10, respectively.

$\frac{1}{\tau_{Al_2O_3}} = \frac{1}{\tau_{1/\epsilon(Al_2O_3)}}$  
(S6)

$\frac{1}{\tau_{TiO_2}} = \frac{1}{\tau_{1/\epsilon(Al_2O_3)}} + \frac{1}{\tau_{e-\text{inj}}} = \frac{1}{\tau_{1/\epsilon(TiO_2)}}$  
(S7)

$\Phi_{e-\text{inj}} = \frac{\tau_{TiO_2}}{\tau_{e-\text{inj}}} = 1 - \frac{\tau_{TiO_2}}{\tau_{Al_2O_3}}$  
(S8)

$\frac{1}{\tau_{OMeTAD}} = \frac{1}{\tau_{1/\epsilon(Al_2O_3)}} + \frac{1}{\tau_{h-\text{inj}}} = \frac{1}{\tau_{1/\epsilon(OMeTAD)}}$  
(S9)

$\Phi_{h-\text{inj}} = \frac{\tau_{OMeTAD}}{\tau_{h-\text{inj}}} = 1 - \frac{\tau_{OMeTAD}}{\tau_{Al_2O_3}}$  
(S10)

where $\tau_{AlO_3}$ is the lifetime of the observed photoluminescence decay for $Al_2O_3$-MAPbI$_3$, $\tau_{TiO_2}$ is the lifetime of the observed photoluminescence decay for TiO$_2$-MAPbI$_3$, $\tau_{OMeTAD}$ is the lifetime of the observed photoluminescence decay for $Al_2O_3$-MAPbI$_3$-OMeTAD, $\tau_{e-\text{inj}}$ is the electron injection rate, $\tau_{h-\text{inj}}$ is the hole injection rate, $\Phi_{e-\text{inj}}$ is the electron injection yield, and $\Phi_{h-\text{inj}}$ is the hole injection yield.

2.4 Spectroelectrochemical measurements
Spectroelectrochemical technique was employed to observe a spectrum of absorption by electrons in the TiO$_2$ conduction band under an application of negative bias into the bare TiO$_2$ electrode. The measurements were conducted with the similar method reported previously.$^8$, $^{12}$ The experiments were performed in a three-electrode electrochemical cell with a quartz optical window using a potentiostat (Ivium Technologies B.V., Compact Stat). The TiO$_2$ nanocrystalline film was prepared on the FTO substrate, and used as a working electrode, attached to the cell window. A platinum wire electrode and a Ag/AgCl electrode were used as a counter and reference electrode, respectively. The photoelectrochemical cell was placed in a UV-VIS-NIR absorption spectrometer (JASCO, V670). Absorption difference spectra were measured by monitoring intensity change of the probe light passing through the TiO$_2$ film electrode in the cell containing 0.1 M lithium perchlorate (supporting electrolyte) in deuterated acetonitrile, after the bias application into the TiO$_2$ film electrode for approximately 5 min. The bias was applied from 0 V with +0.1 V steps, following the measurement of the reference line after 15 min stabilization at 0 V vs. Ag/AgCl.

2.5 Electron microscopy measurements and XRD measurements

Electron microscopy images of Al$_2$O$_3$-MAPbI$_3$ and TiO$_2$-MAPbI$_3$ were obtained by JEOL JEM-6500F scanning electron microscopy (SEM) operated at 10 kV at Institute of Advanced Energy, Kyoto University.

X-ray diffraction patterns were obtained by Rigaku RINT2500 at Institute for Chemical Research, Kyoto University. Data was collected at room temperature using Cu Kα radiation ($\lambda = 1.54178$ A) with a potential of 60 kV and a current of 300 mA.
3. Results

3.1 Solar cell performance

Fig. S1 shows current density – voltage ($J – V$) curves and an IPCE spectrum of the fabricated solar cell. With the forward bias scan, the short circuit photocurrent, $J_{sc}$, is 20.1 mAcm$^{-2}$, the open circuit voltage, $V_{oc}$, is 1.01 V, and the fill factor, $FF$, is 0.71, resulting in an energy conversion efficiency of 14.4 %, while an energy conversion efficiency of 14.7 % was achieved with $J_{sc}$ of 19.7 mAcm$^{-2}$, $V_{oc}$ of 1.01 V and $FF$ of 0.74 by scanning the bias voltage to the reverse direction. This observation has reproduced the result reported recently.$^{13}$

![Fig. S1](image)

**Fig. S1.** (a) $J – V$ curve and (b) IPCE spectrum of the perovskite solar cell. The $J – V$ measurements were performed under AM1.5G solar simulated light, 100 mW cm$^{-2}$ at 25 ± 2 °C or without light irradiation (in dark). The voltage was applied to forward and reverse directions. The IPCE spectrum is not corrected for reflection at the glass surface and at the interfaces.
3.2 Electron microscopy measurements and XRD measurements

Scanning electron microscope images of Al$_2$O$_3$-MAPbI$_3$ and TiO$_2$-MAPbI$_3$ are shown in Figs. S2a and S2b. In both cases, MAPbI$_3$ crystals are formed on top of nanocrystalline metal oxide film. The number of crystals seems higher for Al$_2$O$_3$-MAPbI$_3$, however the crystal size appears to be similar (several hundred nm), being relatively large from the preparation with low PbI$_2$ concentration (0.2 M). The similar low concentration crystal growth was previously observed by Park et al.\textsuperscript{14} By comparing the surface of these films microscopically, the surface morphology is essentially indistinguishable.

X-ray diffraction patterns were observed for Al$_2$O$_3$-MAPbI$_3$ and TiO$_2$-MAPbI$_3$ with reference to their respective metal oxide nanoporous film alone. The results are shown in Figs. S2c and S2c. The diffraction pattern obtained for the nanocrystalline Al$_2$O$_3$ film can be mainly indexed to the orthorhombic $\gamma$-AlOOH (boehmite) phase (JCPDS No. 21-1307)\textsuperscript{15-17} in addition to cubic $\gamma$-Al$_2$O$_3$ phase.\textsuperscript{15, 17, 18} The pattern for the nanocrystalline TiO$_2$ film typically indicates anatase structure.\textsuperscript{19} The diffraction patterns of both Al$_2$O$_3$-MAPbI$_3$ and TiO$_2$-MAPbI$_3$ indicate a tetragonal MAPbI$_3$ phase in addition to $\gamma$-AlOOH/$\gamma$-Al$_2$O$_3$ phase and anatase structure, respectively, in agreement with the previous reports.\textsuperscript{10, 13} Note that we do not see any sign of PbI$_2$ crystal formation for both Al$_2$O$_3$-MAPbI$_3$ and TiO$_2$-MAPbI$_3$, suggesting complete conversion to perovskite.\textsuperscript{13} These observations suggest that the morphology and crystal structure of MAPbI$_3$ are not influenced by the type of metal oxide nanostructure.
Fig. S2. SEM images of Al$_2$O$_3$-MAPbI$_3$ (a) and TiO$_2$-MAPbI$_3$ (b) observed at 10 kV. X-ray diffraction patterns of a nanocrystalline Al$_2$O$_3$ film and Al$_2$O$_3$-MAPbI$_3$ (c) and a nanocrystalline TiO$_2$ film and TiO$_2$-MAPbI$_3$ (d). Peaks from MAPbI$_3$ are shown as asterisks.
3.3 Steady state photoluminescence measurements

Steady state photoluminescence spectra were measured for Al$_2$O$_3$-MAPbI$_3$ and TiO$_2$-MAPbI$_3$ to estimate the upper limit of an electron injection yield (from the excited perovskite to the TiO$_2$ conduction band). The results are compared in Fig. S3a. TiO$_2$-MAPbI$_3$ shows clear emission quench, compared to Al$_2$O$_3$-MAPbI$_3$. The photoluminescence was integrated, and the amount of detected photons were compared between Al$_2$O$_3$-MAPbI$_3$ and TiO$_2$-MAPbI$_3$ to estimate an electron injection yield as photoluminescence quenching efficiency. The estimated injection yield is 85 %, indicating that the rate is approximately one order of magnitude faster than the excited state lifetime.

Fig. S3. (a) Photoluminescence spectra of Al$_2$O$_3$-MAPbI$_3$ and TiO$_2$-MAPbI$_3$ with 625 nm excitation. (b) Photoluminescence spectra of Al$_2$O$_3$-MAPbI$_3$ and Al$_2$O$_3$-MAPbI$_3$-OMeTAD with 625 nm excitation. The photoluminescence spectra were normalized with the number of absorbed photons at the excitation wavelength.
A hole injection yield was estimated in the similar manner using the data from \( \text{Al}_2\text{O}_3\)-MAPbI\(_3\) and \( \text{Al}_2\text{O}_3\)-MAPbI\(_3\)-OMeTAD. In this case, only a hole transfer reaction from the perovskite valence band to the OMeTAD is expected, while no electron injection occurs. The result is shown in Fig. S3b. By coating an OMeTAD layer on top of the perovskite layer, photoluminescence was remarkably quenched, indicating 96% hole injection yield.

### 3.4 Transient emission measurements

Transient photoluminescence spectroscopy was employed to assess dynamics of an electron injection process (from the perovskite to the TiO\(_2\) conduction band), since this spectroscopy is sensitive to detect change in low photoluminescence intensity at the low excitation intensity (typically 0.01 \(\mu\text{J/cm}^2\)). A wide range of excitation intensities (0.01 ~ 50 \(\mu\text{J/cm}^2\)) was introduced to monitor their influence on the dynamics. Excitation intensity dependence of photoluminescence dynamics for TiO\(_2\)-MAPbI\(_3\) was observed. The results are shown in Fig. S4a. Similar to the decays obtained for Al\(_2\)O\(_3\)-MAPbI\(_3\) (Fig. 2a), the increase of the excitation intensity results in acceleration of the photoluminescence decay dynamics. These decay kinetics were analyzed using Equation S3 above.
Fig. S4. (a) Excitation intensity dependence of transient emission (perovskite excited state) decays obtained for TiO$_2$-MAPbI$_3$ with 625 nm excitation. The number in the figure presents excitation intensity (unit: $\mu$J/cm$^2$), and the line shows a result of fitting with Equation S3. (b) Comparison of transient emission decays of Al$_2$O$_3$-MAPbI$_3$ (dark red dots: data, line: fitted result) and TiO$_2$-MAPbI$_3$ (dark blue dots: data, line: fitted result). The solid line indicates results of fitting with Equation 1 and S3, respectively.

The photoluminescence decay dynamics were compared with those for Al$_2$O$_3$-MAPbI$_3$. As shown in Fig. S4b, a clear acceleration of the photoluminescence decay is observed for TiO$_2$-MAPbI$_3$ with 50 nJ/cm$^2$ excitation. This acceleration is owing to an electron injection process from the excited perovskite to the TiO$_2$ conduction band. Even with the higher excitation intensity (2.3 $\mu$J/cm$^2$), slight acceleration of photoluminescence decays was observed. These data suggest that the electron injection process is one of the major paths to quench the photoluminescence.
The electron injection yield ($\Phi_{\text{inj}}$) was estimated using Equation S8. With the excitation intensity of 50 nJ/cm$^2$, the calculated electron injection yield is 90%. In contrast, the excitation intensity of 2.3 $\mu$J/cm$^2$ decreased the electron injection yield to 37%. This result suggests that the increase in the excitation intensity decreases an electron injection yield.

3.5 Transient absorption measurements of N3 sensitized TiO$_2$ films

The same TiO$_2$ film was employed to monitor charge recombination dynamics at N3 dye/TiO$_2$ interface. An absorption spectrum of the N3 sensitised TiO$_2$ film is shown in Fig. S5a. A transient absorption spectrum of this film was obtained at 2 $\mu$s after 625 nm excitation (Fig. S5b). This spectrum essentially indicates charge separated states. Following the previous report, the absorption around 800 nm is assigned to N3 dye oxidized state, while the absorption at a 1,200~2,500 nm range was resulting from absorption by the injected electrons in the TiO$_2$ conduction band or surface states.\textsuperscript{20} A transient absorption decay is shown in Fig. S5c. Slightly accelerated dynamics was observed for charge recombination between a dye oxidized state and an electron in the TiO$_2$ with the half lifetime of approximately 150 $\mu$s (stretched parameter, $\alpha$, = 0.36), compared to the reported data.\textsuperscript{20} The difference probably originates from the thinner TiO$_2$ film thickness (thickness: 2.8 $\mu$m) we employed here, as the increased number of the injected electrons in the TiO$_2$ results in faster charge recombination dynamics.\textsuperscript{21, 22} Here we employ this decay dynamics to compare charge recombination dynamics observed for TiO$_2$-MAPbI$_3$. 
Fig. S5. (a) Absorption spectrum, (b) transient absorption spectrum, and (c) transient absorption decay of N3 dye sensitized TiO$_2$ films. The fitted line using a stretched exponential function is shown as a black line in Fig. S5c. The transient absorption spectrum and decay were obtained at 2 μs and at 1,600 nm (probe wavelength), respectively, after 700 ps pulse excitation at 625 nm.
3.6 Spectrochemical and spectroelectrochemical measurements of spiro-OMeTAD oxidized states and electrons in TiO$_2$ conduction band spectra

The oxidized state of spiro-OMeTAD was prepared by adding tris[2-(1H-pyrazol-1-yl)-4-tert-butylpyridine]cobalt(III) tris[bis(trifluoromethylsulfonyl)imide]$^6$ into spiro-OMeTAD solution (CH$_2$Cl$_2$). The results are shown in Fig. S6. The spectrum of absorption by electrons accumulated in the TiO$_2$ conduction band was created spectroelectrochemically by applying electrical bias into the TiO$_2$ electrode. The absorption difference spectrum from the spectra between -0.9 and -1.0 V is shown in Fig. S6. The addition of these two spectra between 1,100 and 2,500 nm is also shown in Fig. S6. The amplitude increase around 2,500 nm was clearly observed, compared to the OMeTAD oxidized state spectrum.
**Fig. S6.** Absorption spectra of spiro-OMeTAD oxidized state and electrons in the TiO$_2$ conduction band. The addition of these spectra between 1,100 and 2,500 nm is also shown (black line). The spikes at 2,250 and 2,380 nm originate from absorption by the solvent or the electrolyte.
References

Chapter 5 Optimization of Mesoscopic CH$_3$NH$_3$PbI$_3$ Perovskite Cell Structure through the Study of Thickness Controlling Interfacial Charge Transfer Dynamics

Introduction

During the past few years, organic-inorganic trihalide perovskite solar cells have been widely investigated as one of most promising candidates for photon-to-electron conversion. The power conversion efficiency of perovskite solar cells dramatically and swiftly increases up to date 22.1%, showing aggressive competitiveness with other new generation photovoltaic devices even with conventional silicon solar cells. A typical perovskite solar cell employs a perovskite layer sandwiched by p-type semiconductor (such as spiro-OMeTAD, PEDOT or NiO) and n-type semiconductor (such as TiO$_2$, ZnO or PCBM) layers. Following light absorption, an electron and a hole are separated at the perovskite film interface, and will be collected at the back electrodes. Based on this simple configuration, it is clear that the perovskite interface controls the cell performance and stability. In the chapter 4, a role of a TiO$_2$ nanocrystalline film acting as an electron acceptor is described.$^1$ The electron injection rate (~10 ns) is relatively slow compared to dye or QD sensitised films,$^{2-3}$ however it is sufficiently fast compared to the excited state lifetime (~200 ns), confirming high charge transfer quantum yield. In addition, as a key factor, photo-excitation intensity has shown significant impact on the perovskite excited state lifetime and charge separation efficiency.
In this chapter, parameters controlling charge separation and recombination dynamics at the perovskite interfaces have been demonstrated by employing a series of transient absorption and emission spectroscopies. These results clearly show that mesoscopic structure is more favourable for efficient electron injection from perovskite into TiO$_2$ nanopores compared to planar heterojunction structure. Furthermore, efficient and swift hole injection from perovskites to spiro-OMeTAD is likely independent on controlled parameters, mainly contributing the overall high-efficiency of MAPbI$_3$-based perovskite devices. Besides, thick perovskite absorber is preferable to effectively suppress the charge recombination due to the formation of complete coverage and pin hole-free layer.

This chapter has been prepared in manuscript and will be soon submitted to Advanced Energy Materials.

References


Optimization of mesoscopic CH$_3$NH$_3$PbI$_3$ perovskite cell structure through the study of thickness controlling interfacial charge transfer dynamics

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Abstract: Perovskite solar cells have been recognized as a newly emerging solar cell with the potential of achieving relatively high efficiency with a low cost fabrication process. In particular, facile solution processed cell fabrication facilitates rapid development of optimum cell structure and composition. A typical perovskite solar cell employs a perovskite layer sandwiched by p-type semiconductor (like spiro-OMeTAD or PEDOT) and n-type semiconductor (like TiO$_2$ or PCBM) layers. Following light absorption, an electron and a hole are separated in the perovskite film, and are collected at the back electrodes. Based on this simple configuration, it is clear that the perovskite interface controls the cell performance and stability. It has been reported a role of a TiO$_2$ nanocrystalline film acting as an electron acceptor. The electron injection rate (~10 ns) is relatively slow compared to dye or QD sensitised films, however it is sufficiently fast compared to the excited state lifetime (~200 ns), confirming high charge transfer quantum yield. In this paper, parameters controlling charge transfer dynamics at the perovskite interfaces are presented by employing a series of transient
absorption and emission spectroscopies. Nanosecond transient emission spectroscopy clarifies charge separation processes, while Vis-NIR submicrosecond-millisecond transient absorption spectroscopies identify charge recombination rates.

1. Introduction

Perovskite solar cells have been recognized as a newly emerging solar cell with the potential of achieving high efficiency with a low cost fabrication process.\textsuperscript{[1]} In particular, facile solution processed cell fabrication facilitated rapid development of optimum cell structure and composition. A typical perovskite solar cell employs a perovskite layer sandwiched by p-type semiconductor (such as spiro-OMeTAD\textsuperscript{[2]}, PEDOT\textsuperscript{[3]} or NiO\textsuperscript{[4]}) and n-type semiconductor (such as TiO\textsubscript{2}\textsuperscript{[5]}, ZnO\textsuperscript{[6]} or PCBM\textsuperscript{[7]}) layers.\textsuperscript{[1h, 1k, 8]} Several different cations including metal and organic cation such as Pb\textsuperscript{2+}, Cs\textsuperscript{+}, Rb\textsuperscript{+}, Sn\textsuperscript{2+}, Sn\textsuperscript{4+}, Bi\textsuperscript{2+} and Sb\textsuperscript{2+}, and methyl ammonium (MA) and formidium ammonium (FA) cations\textsuperscript{[9]} have been investigated to form perovskite strucutre to improve light absorption range and stability. Among them, although originally developed, organic-inorganic perovskite such as MAPbI\textsubscript{3} perovskite in combination with mesoporous TiO\textsubscript{2} film (m-TiO\textsubscript{2}) and PTAA/spiro-OMeTAD shows the highest efficiency reaching 22 % solar to energy conversion efficiency.\textsuperscript{[1g]}

The performance of perovskite solar cells, particularly photocurrent generation, is controlled by charge transfer dynamics at the material interface in the solar cell. Electron and hole injection processes at the n-type semiconductor/perovskite and the perovskite/p-type semiconductor interfaces are the primary charge separation reactions to operate the solar cell.\textsuperscript{[10]} The charge injection yield increases if the charge injection rates are faster than the perovskite excited state decay or the electron-hole recombination inside the perovskite layer following the exciton dissociation.\textsuperscript{[1a, 11]} The charge collection yield at the electrode increases if the recombination of the separated charges (electron and hole) is sufficiently slow. Direct
measurements and comparison of the charge injection and recombination reactions will provide a guide to design a structure of the solar cell. For example, if thickness of an n-type semiconductor layer influences photo-induced electron injection and recombination rates, the optimum thickness can be identified by maximising the electron injection rate and retarding the charge recombination rate. However, such direct measurements of charge injection and recombination dynamics in correlation with the solar cell structure have rarely been conducted.

Structure, morphology, homogenity and quality of each semiconductor layer in the solar cell and cell operation conditions such as irradiation of light wavelength and intensity potentially influence primary charge injection and recombination dynamics, and thus the solar cell performance. Understanding and optimising the influences of these parameters support design of the solar cell structure. For example, we recently reported that increase of MAPbI$_3$ perovskite excitation intensity accelerate electron-hole recombination within the perovskite layer, competing with the electron and hole injection processes, thereby showing that the electron injection and hole injection yields decrease with the light intensity increase.$^{[12]}$ We concluded that an m-TiO$_2$/MAPbI$_3$/OMeTAD film is not suitable to be applied for concentrator PVs, but rather for light sensor devices or PV under 1 sun condition.

From our previous studies and others of an m-TiO$_2$/MAPbI$_3$/OMeTAD film,$^{[13]}$ the electron injection process appears to be slower than the hole injection process, and thus the design of the m-TiO$_2$ film in correlation with the perovskite structure will be of particular importance to identify the most appropriate cell structure. Here we demonstrate the influence of m-TiO$_2$ film and perovskite layer thickness on the charge injection and recombination dynamics directly monitored by transient absorption and emission spectrometers. By comparing these dynamics, we will propose the optimised m-TiO$_2$/MAPbI$_3$ structure to maximise the photocurrent generation.
2. Results

2.1. Difference in interfacial electron transfer dynamics on cell structure

The main difference in the cell structures shown in Schemes 1a and 1b is that the TiO$_2$ particle layer is inserted as an electron acceptor layer in the mesoporous TiO$_2$ based solar cell. To clarify the role of this electron acceptor layer and to elucidate any advantage of the structure against the other, we have compared charge transfer dynamics at perovskite interfaces. The perovskite layer is deposited on a glass (glass/MAPbI$_3$), FTO (FTO/MAPbI$_3$), compact TiO$_2$ (FTO/c-TiO$_2$/MAPbI$_3$) or mesoporous TiO$_2$ film (thickness: 200 nm) with (FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$/OMeTAD) or without (FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$) OMeTAD using PbI$_2$ concentration of 1.1 M. Figure 5.1 shows absorption spectra of FTO/c-TiO$_2$/MAPbI$_3$ and FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$, i.e. comparing perovskite spectra in the presence and absence of mesoporous TiO$_2$ layer. Clearly, the absorption amplitude is similar, suggesting that the optical thickness of the perovskite layer is similar between these two films. This means that the presence of a mesoporous TiO$_2$ layer does not essentially influence the perovskite thickness. The surface morphology of these films is essentially the same, i.e. similar (data are not shown.) to the image shown in Figure 5.2b, suggesting that the presence of a mesoporous TiO$_2$ layer does not also influence the perovskite layer morphology. Absorption spectra of all other films are also similar to these two spectra.

As we previously reported,$^{[12]}$ and discussed in the experimental section, photo-induced electron and hole injection reactions can be observed by acceleration of perovskite photoluminescence decay. Figure 5.1b compares photoluminescence decays of glass/MAPbI$_3$, FTO/MAPbI$_3$ and FTO/c-TiO$_2$/MAPbI$_3$. The perovskite excited state decay was observed for glass/MAPbI$_3$ (lifetime: 34 ns), while rapid acceleration of the decay was observed for FTO/MAPbI$_3$, indicating that rapid electron and/or hole injection occurs from the perovskite to the FTO. Following the analysis described in the experimental section, the estimate electron and/or hole injection rate is 1.7 ns using Equation 8. In contrast, slight decay
acceleration was observed for FTO/c-TiO₂/MAPbI₃, indicating that the electron injection from the perovskite to the compact TiO₂ is slow. The estimate electron injection rate is 160 ns, using Equation 6 in the experimental section. This slow electron injection rate suggests that the current compact TiO₂ layer may not be suitable as an electron acceptor layer if the electron injection is the rate limiting process in the perovskite solar cells. Our observation is consistent with previous report[14] which indicated that c-TiO₂/MAPbI₃ even exhibited enhanced transient emission lifetime compared with that of only MAPbI₃ film, owing to the potential barrier caused by electron accumulation at the interface.

Figure 5.1c compares photoluminescence decays of glass/MAPbI₃, FTO/c-TiO₂/m-TiO₂/MAPbI₃ and FTO/c-TiO₂/m-TiO₂/MAPbI₃/OMeTAD. Clear acceleration of photoluminescence decay was observed for FTO/c-TiO₂/m-TiO₂/MAPbI₃, indicating that electron injection from the perovskite to the mesoporous TiO₂ is significantly faster (injection rate: 11 ns using Equation 6 than the electron injection from the perovskite to the compact TiO₂. This observation is plausible, as most of excited light is absorbed by the perovskite inside the mesoporous TiO₂ structure, and thus the generated electron inside the perovskite can reach the TiO₂ particle surface without long diffusion distance (pore size: 20 nm on average).[15] Further acceleration was observed for FTO/c-TiO₂/m-TiO₂/MAPbI₃/OMeTAD, suggesting that the hole injection from the perovskite to the OMeTAD is even faster (injection rate: 1.9 ns using Equation 8). These observations are consistent with our previous report.[12] Charge injection yields to the electron donor and acceptors (c-TiO₂, m-TiO₂ and OMeTAD) were estimated as a function of excitation intensity using Equation 12 or 14 in the experimental section, and presented in Figure 5.1d. The hole injection yield is higher than the electron injection yield, while the electron injection yields to compact TiO₂ are low (<20%) at any excitation intensity. We have also confirmed these electron and hole injection yields by comparing the amplitudes of photoluminescence spectra obtained for glass/MAPbI₃, FTO/c-TiO₂/m-TiO₂/MAPbI₃ and FTO/c-TiO₂/m-TiO₂/MAPbI₃/OMeTAD (data are not shown),
essentially in agreement with the calculated charge injection yields from the photoluminescence decay data. These results suggest that photocurrent generation in perovskite solar cells is essentially controlled by the hole injection yield, but not by the electron injection process. The fact that the photocurrent values of the mesoporous TiO$_2$ based perovskite and the planar structure perovskite solar cell are similar ($J_{SC}$: >20 mA/cm$^2$), the electron injection processes (to the mesoporous TiO$_2$ or compact TiO$_2$) are not the rate controlling process in the photocurrent generation. In other words, the photocurrent generation is insensitive to the electron injection rate.

2.2. Influence of perovskite layer thickness upon charge transfer dynamics

Since the role of the mesoporous TiO$_2$ layer is clarified, we now investigate influence of the perovskite layer thickness (on top of the mesoporous TiO$_2$ layer) on charge transfer dynamics in the mesoporous TiO$_2$ based perovskite films. We found that the perovskite thickness on top of the mesoporous TiO$_2$ layer (thickness: 200 nm) can be controlled by concentration of PbI$_2$ solution during the perovskite film preparation (see the experimental for the detail).

Figure 5.2a shows absorption spectra of the perovskite films prepared by altering PbI$_2$ solution concentration. The spectral shapes are almost identical, but the absorption amplitude increases with the increase of the PbI$_2$ solution concentration. The perovskite thickness was assessed by the cross-sectional SEM image, and is 100, 200, 280 and 300 nm (on average), prepared with the PbI$_2$ solution concentration of 0.2, 0.5, 1.0 and 1.1 M, respectively, which is consistent with previous reports for the relationship between PbI$_2$ precursor concentration and resultant perovskite layer thickness.$^{[16]}$

Figure 5.2b shows surface SEM images of perovskite layers deposited on the mesoporous TiO$_2$ layer, prepared with PbI$_2$ concentration of 0.2 and 1.1 M. The film prepared with 0.2 M PbI$_2$ shows homogeneous perovskite layer with several large perovskite crystals with a
diameter of several hundreds nm, while the film prepared with 1.1 M PbI$_2$ shows lots of large perovskite crystals deposited on top of the mesoporous TiO$_2$ film, i.e. most of the film surface is covered by the large perovskite crystals. The similar observation was reported by Park et al.$^{[16b]}$ The SEM observations suggest that the increase of PbI$_2$ concentration essentially increases the number of large crystals. One of the SEM cross-sectional images (for the film prepared with 1.1 M PbI$_2$) is shown in Figure 5.2c. The large crystals grown on the mesoporous TiO$_2$ film are clearly seen, which is similar as the previous observation for the complete coverage of large perovskite crystals on top of mesoporous TiO$_2$ nanopores commonly generated from high concentration of PbI$_2$ precursor.$^{[16a, 16b]}$

Photoluminescence decay studies for the film with various perovskite thickness were conducted. However, we found that for a film prepared with 0.2 M PbI$_2$ (the thinnest perovskite), transient absorption study can be performed using visible nanosecond transient absorption spectroscopy, since the film absorbance is relatively low, i.e. the probe light can partially be transmitted, and the transient change of the probe light can be monitored. Figure 5.3a shows visible to infrared transient absorption spectra for the mesoporous TiO$_2$ based perovskite films, prepared with 0.2 M PbI$_2$ with (FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$/OMeTAD) and without (FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$) OMeTAD, observed at 2 μs after 625 nm excitation. For the FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$, the residual transient emission is observed around 760 nm, in agreement with the steady state emission spectrum. No obvious transient absorption at near infrared wavelengths is observed, i.e. no sign of the electron injection reaction is observed. Previously we reported that a low electron injection yield (<10 %) is expected with relatively strong excitation energy of 120 μJ cm$^{-2}$. Also, the extinction coefficient of an electron in the TiO$_2$ is small (~3400 M$^{-1}$cm$^{-1}$). Thus, the contribution of the absorption by the electrons in the TiO$_2$ is negligible, and the small signal of the injected electrons is hidden within the noise level of the detector. In contrast, the large absorption with a wide band width was observed at 1,000 ~ 2,500 nm for FTO/c-TiO$_2$/m-
TiO$_2$/MAPbI$_3$/OMeTAD. The OMeTAD oxidized state with the absorption peak at 1,600 nm is also shown in Figure 5.3a. This oxidized state was chemically created (see the experimental for the detail). These positive spectral shapes are almost identical, and thus the transient spectrum indicates charge separated state following the hole injection. Note that the transient absorption amplitude around 500 nm is significantly smaller compared to that of the OMeTAD oxidized state. The amplitude was decreased owing to the ground state bleach (negative amplitude).

Figure 5.3b shows nanosecond transient absorption signal observed at 500 nm. This transient growth was fitted with a single exponential with two different components (1.2 and 23 ns). As we reported previously, we estimate that the hole injection,$^{[12]}$ and thus the electron injection yield with excitation intensity of 120 $\mu$J cm$^{-2}$ is 40~50 %. Also we expect the fast excited state decay with the relatively high excitation intensity of 120 $\mu$J cm$^{-2}$. Therefore, it is reasonable to consider that the rapid signal decay observed on early nanosecond scale, the faster component, originates mainly from the mixture of the perovskite excited state decay and the hole injection (signal growth by generation of the OMeTAD oxidized state). In this transient signal it is not easy to distinguish the component of the excited state decay from the hole injection component, however it is clear that the hole injection occurs faster than 3 ns, in agreement with the data shown in Figure 5.1c. As discussed above, we believe that the contribution of the absorption by the electrons in the TiO$_2$ is small owing to the low extinction coefficient ($\sim$3400 M$^{-1}$cm$^{-1}$). The slower component, i.e. the 2$^{nd}$ component, therefore originates from the recovery of the ground state bleach concomitant with the electron injection reaction.

The influence of the perovskite layer thickness on the electron injection dynamics is shown in Figure 5.4a. The excited state decay obtained for glass/MAPbI$_3$ (prepared with 1.1 M PbI$_2$) under the same excitation condition is shown as reference. We found that the decay rate is similar for glass/MAPbI$_3$ prepared using a different concentration of PbI$_2$ solution over
0.2~1.1 M (data are not shown). The electron injection rate becomes faster with the thinner perovskite layer thickness. For the film prepared with 0.2 M PbI$_2$ solution, the majority of the excitation light was absorbed by the perovskite inside the mesoporous TiO$_2$ structure, implying that the photo-generated electrons travel within 10 nm (average pore size: 20 nm)$^{[15]}$ before reaching the TiO$_2$ surface. We therefore expect the faster electron injection rate. In contrast, for the films prepared with the high concentration PbI$_2$ solution (1.0 or 1.1 M), some of the excitation light are absorbed by the perovskite crystals formed on top of the mesoporous TiO$_2$ film, considering the excitation wavelength of 625 nm, suggesting that the photo-generated electrons have to travel/diffuse a long distance to reach the TiO$_2$ surface, resulting in the slower electron injection rates.

Transient charge recombination dynamics are monitored for m-TiO$_2$/MAPbI$_3$/OMeTAD with various perovskite layer thickness at 1,600 nm (decays of the OMeTAD oxidized state), and the results are shown in Figure 5.4b. All of the decays were fit with the stretched exponential function with a stretched parameter of 0.3~0.5, in agreement with the previous report.$^{[12]}$, suggesting that the charge recombination processes are essentially dominated by the multiple trapping of electrons in the TiO$_2$,$^{[12,17]}$ assuming no influence from the hole trap states in the OMeTAD, if there are. For the perovskite film thickness up to 200 nm, the recombination lifetime is essentially the same (~1 ms), while the lifetime was significantly retarded by nearly two orders of magnitude up to 40 ms for the film with thicker perovskite layer. Similar to the discussion above, by increasing PbI$_2$ solution concentration, the larger perovskite crystals were formed on top of the mesoporous TiO$_2$ film (Figure 5.2b). We speculate that the charge recombination occurs via the large perovskite crystal for the films prepared using the high PbI$_2$ solution concentration (1.1 M), i.e. the recombination rate is significantly retarded. For the film prepared with less PbI$_2$ solution concentration, the charge recombination occurs where no large crystal is present, i.e. where the OMeTAD layer is almost directly deposited on top of the mesoporous TiO$_2$ film.
The perovskite film thickness dependence on the electron and hole injection yields and charge recombination lifetimes are summarized in Figure 5.4c and Table 5.1. The hole injection yields were obtained by comparing the amplitudes of the steady state emission spectra for Al₂O₃/MAPbI₃ and Al₂O₃/MAPbI₃/OMeTAD (Figure S5.1). The electron injection yields slightly decreased by exciting some large crystals, while the hole injection yields are over 95%, irrelevance of the presence of the large perovskite crystals. The charge recombination is significantly retarded, as most of the film surface was covered by the large perovskite crystals.

In terms of the prolonged charge recombination effective lifetime with the growth of perovskite thickness, it is strongly recommended that thick perovskite film should be utilized as the active layer of photovoltaic device to obtain optimum charge separation/recombination dynamics and abundant light harvesting.

2.3. Influence of mesoporous TiO₂ film thickness upon charge transfer dynamics

Here we investigate influence of mesoporous TiO₂ (m-TiO₂) film thickness on charge separation and recombination dynamics. We employed two extremely different film thicknesses, a 2.8 μm thick (using the screen printing method) and a 150 nm thick TiO₂ film (using the spin coating method) to compare the dynamics. To obtain relatively homogeneous excitation condition, a low PbI₂ precursor concentration (0.2 M) was used to form the perovskite layer.

Figure 5.5a shows photoluminescence decays for perovskite deposited thick and thin m-TiO₂ films (without OMeTAD layer) in comparison with the perovskite excited state decay (obtained from glass/MAPbI₃). Although slight difference in dynamics can be seen with the film thickness, the presence of m-TiO₂ accelerates photoluminescence decay rates, that is, the electron injection process is significantly faster than the excited state decay. We have also investigated excitation intensity dependence on photoluminescence decays for these films.
The excited state lifetimes as a function of excitation intensity are shown in Figure S5.2. The electron injection yields are estimated using Equation 12, and the results are summarized in Figure 5.5b. Generally slightly higher electron injection yields can be expected using a thinner m-TiO₂ film. Although the origin of this slight difference is not clear, it is clear that higher electron injection yields are obtained in the presence of m-TiO₂ structure, compared to the perovskite film deposited on the dense TiO₂ layer (Figure 5.1d). This observation is reasonable, since only the perovskite domains inside the mesoporous TiO₂ structure are excited, and thus the excited electron in the perovskite travels only up to 10 nm (assuming that the pore size is 20 nm) to inject an electron to the TiO₂.

The hole injection yields were estimated by comparing the amplitude of the photoluminescence spectra obtained for these films shown in Figure S5.1b. Influence of the m-TiO₂ film thickness on the electron and hole injection yields are summarised in Figure 5d. Surprisingly, the hole injection yield is insensitive to the TiO₂ film thickness, although the generated holes inside the perovskite domain close to the glass substrate have to travel for a long distance to reach the OMeTAD layer, in another word, the perovskite layer rather functions as a hole conductor to facilitate the remaining holes to efficiently diffuse to the OMeTAD layer.[18] Above all, we conclude that both electron and hole injection yield exceed 90 %, and insensitive to the m-TiO₂ film thickness.

Figure 5.5c compares charge recombination dynamics for these TiO₂ films in the presence of OMeTAD layer. The OMeTAD layer were prepared the identical condition described in the experimental section. Both decays show multi-exponential dynamics, suggesting that the multiple electron trapping inside the TiO₂ influences the recombination rates. However, the lifetime obtained from the streched exponential analysis indicates about 7 times slower for the thicker film, compared to that for the thinner film. The observation of this retardation is reasonable, since the electrons injected to the TiO₂ structure close to the glass substrate have
to travel longer distance inside the TiO$_2$ film to reach the location close to the OMeTAD layer where the injected holes are located.

Figure 5.5d summarises the comparison of charge injection yields and charge recombination rates between the thicker and thinner TiO$_2$ film. Both electron and hole injection yields are insensitive to the TiO$_2$ film thickness, while the charge recombination is retarded by increasing the TiO$_2$ film thickness.

In addition, Kim and coworkers$^{[8c]}$ has concluded that by increasing mesoporous TiO$_2$ thickness in perovskite solar cell, the dark current and electron transport resistance seriously increase in terms of impedance spectroscopic study, consistent with our observed fastened electron injection rate in perovskite deposited film with thin porous TiO$_2$ layer.

3. Discussion

In the present study, we have investigated influence of the perovskite layer and mesoporous TiO$_2$ film thickness on the charge separation and recombination dynamics. The electron injection yield decreases with increase of the perovskite layer thickness, however almost invariant with the mesoporous TiO$_2$ film thickness. The absence of the mesoporous TiO$_2$ film significantly decreases the electron injection yield. In contrast, the hole injection yield remains high (>95 %) with the perovskite layer thickness of up to 300 nm, and from the absence of TiO$_2$ film to TiO$_2$ film of 2.8 µm. As the hole diffusion length of 110 nm$^{[19]}$, the hole transport completes within ps over the perovskite layer of 2.8 µm. We therefore conclude that the charge separation at the perovskite interfaces is essentially controlled by the hole injection process, i.e. the charge separated states are formed by the fast hole injection rate and efficiency, irrelevance of perovskite layer and TiO$_2$ film thicknesses.

We have observed that the charge recombination rate is retarded by increasing TiO$_2$ film thickness from 150 nm to 2.8 µm, while increasing perovskite thickness from 100 to 300 nm increased the charge separated lifetime by nearly two orders of magnitude. This retardation
clearly suggests that the perovskite layer acts as a blocking layer for the path of charge recombination process.

From the present kinetic study, employing FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$/OMeTAD/Au solar cell structure, we conclude that the cell performance is essentially controlled by the charge recombination process, \textit{i.e.} longer charge separated state lifetime potentially improves solar cell performance. With the current materials to fabricate solar cells shown in Scheme 1c, here we propose the best cell structure. The optimal performance will potentially be obtained by decreasing $d_{p-TiO_2}$ as thin as possible, although this m-TiO$_2$ layer has to be present (to increase the electron injection yield), and by increasing $d_{\text{perovskite}}$ as thick as possible, provided that the thickness is less than 350 nm$^{[20]}$.

4. Conclusion

In this study, charge carriers (electron and hole) transfer dynamics at the interfacial area between MAPbI$_3$ and charge extraction materials, \textit{i.e.} ETM (nanocrystalline TiO$_2$ film) and HTM (spiro-OMeTAD), have been comprehensively investigated by using transient photoluminescence spectroscopy and transient absorption spectroscopy. The mesoscopic structure indicates a significantly enhanced electron injection yield from perovskite to mesoporous TiO$_2$ conduction band compared to the planar heterojunction structure only with compact TiO$_2$ layer, although an extremely high hole injection yield can be attained from perovskite to spiro-OMeTAD which is independent on the structure. For the mesoscopic structure, the dependence of charge transfer dynamics has been illustrated on several identified factors, including thickness of perovskite layer and thickness of mesoporous TiO$_2$ film. The dynamic control at the interfaces of p-TiO$_2$/perovskite/OMeTAD could be crucial for the optimization of charge separation/recombination processes. Based on our results, it is recommended to employ highly thick perovskite layer, a thin thickness of mesoporous TiO$_2$ film and high quality of HTM such as doped spiro-OMeTAD, which can potentially obtain
nearly 100% of charge injection yield (electron and hole) and realize extremely long-lived charge recombination dynamics under one sun condition. Undoubtedly, once the charge transfer process is kinetically managed, the performance of perovskite solar cell will be predicted to improve.

5. Experimental Section

Materials: Dehydrated PbI\textsubscript{2} and CH\textsubscript{3}NH\textsubscript{3}I (MAI) powder were purchased from Tokyo Chemical Industry, CO., LTD. (TCI). \textit{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, H\textsubscript{2}O < 8 ppm). 2,2',7,7'-Tetrakis(\textit{N,N}-di-\textit{p}-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) was purchased from Merck. Titanium di-isopropoxide bis(acetylacetonate) was purchased from Sigma-Aldrich Co. LLC. A nanocrystalline TiO\textsubscript{2} paste (PST-18NR, anatase, particle diameter: ca. 20 nm) for spin coating and screen printing was obtained from JGC C&C. Al\textsubscript{2}O\textsubscript{3} powder (Aeroxide Alu C, particle diameter: approximately 13 nm) was provided by Evonik Degussa GmbH.

Sample preparation: A CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite layer was deposited on a various different substrate. The substrate includes a slide glass (glass/MAPbI\textsubscript{3}), a fluorine doped tin oxide (FTO, 15 mm × 25 mm) glass (FTO/MAPbI\textsubscript{3}), a nanocrystalline Al\textsubscript{2}O\textsubscript{3} film prepared on a slide glass (Al\textsubscript{2}O\textsubscript{3}/MAPbI\textsubscript{3}), a compact TiO\textsubscript{2} layer prepared on FTO (FTO/c-TiO\textsubscript{2}/MAPbI\textsubscript{3}), or a nanocrystalline TiO\textsubscript{2} film with (FTO/c-TiO\textsubscript{2}/m-TiO\textsubscript{2}/MAPbI\textsubscript{3}/OMeTAD) or without (FTO/c-TiO\textsubscript{2}/m-TiO\textsubscript{2}/MAPbI\textsubscript{3}) OMeTAD. A compact TiO\textsubscript{2} layer (c-TiO\textsubscript{2}) was deposited on a FTO substrate by spray pyrolysis of 0.05 M titanium di-isopropoxide bis(acetylacetonate) solution in ethanol at 450 °C.\textsuperscript{[21]}
Al₂O₃ nanocrystalline films (thickness: 3.0 µm) were prepared by the same screen printer with the different printing mask, using a home-made Al₂O₃ paste, following the previously reported method. The printed Al₂O₃ films were calcined at 500 °C for 1 h in an air flow oven. A transparent TiO₂ nanocrystalline film was prepared on the as-prepared compact TiO₂ layer or a slide glass. The film thickness was controlled by depositing with two different methods, spin coating and screen printing methods. A thin transparent TiO₂ nanocrystalline film (thickness: 150 nm) was deposited by spin coating at 5000 rpm for 30 s using an ethanol suspension of TiO₂ paste (TiO₂ paste:ethanol = 1:3.5 wt. ratio). A thick transparent TiO₂ nanocrystalline film (thickness: 2.8 µm) was prepared by the screen printing method with the TiO₂ paste. The film, after printing, was leveled for 15 min, 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+), and confirmed by observing a cross-section image using scanning electron microscope (JEOL JEM-6500F) with an operating voltage of 10.0 kV.

A CH₃NH₃PbI₃ perovskite layer was deposited on a various different film or sustrate, as discussed above, inside a glove box, following the reported method. A PbI₂ solution with various concentration (0.2-1.1 M) 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 into a perovskite layer. To remove excess amount of MAI, the films were quickly rinsed with 2-propanol and dried at 70 °C for 30 min. For some films, a hole-transporting layer was deposited on top of TiO₂-MAPbI₃ and Al₂O₃-MAPbI₃ by spin-coating a solution of OMeTAD in dehydrated chlorobenzene (0.058 M). The film was fixed 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.
Characterization:

**Optical measurements.** Absorption spectra of perovskite deposited films were measured by a UV-Vis absorption spectrometer (Shimadzu, UV-2450). Photoluminescence spectra of the film were collected using a PTI UV-Vis fluorometer (Photon Technology International, Inc.) with slit widths 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.

Nanosecond transient emission spectroscopy (ns-TES) was employed to monitor perovskite excited state decay dynamics. An electron injection from the perovskite excited state to the TiO$_2$ was also measured by following the emission quenching dynamics compared to the excited state decays observed for MAPbI$_3$ on a slide glass or nanocrystalline Al$_2$O$_3$ film. Data were obtained by a home-built transient emission spectrometer with an N$_2$ laser (LTB Lasertechnik Berlin GmbH, MNL 202-C) pumped dye laser (LTB Lasertechnik Berlin GmbH, ATM200, 700 ps pulse duration) as an excitation source. The excitation laser pulse was irradiated from the glass substrate side. Emission from a perovskite layer was collected through a monochromator (Acton, Princeton Instruments), and detected by a nanosecond detection system (Unisoku Co., Ltd., TSP-2000SN, time resolution: 1.2 ns (FWHM)) with a fast oscilloscope (Tektronix, TDS 3052C, Digital Phosphor Oscilloscope 500 MHz 5 GS/s) at 10 Hz excitation repetition rate. The emission decay profile was synchronized with the excitation pulse and the detection system using a laser trigger detector.

Nanosecond visible transient absorption spectroscopy (ns-TAS) was employed to monitor charge separation dynamics. The measurements were conducted by a home-built transient absorption spectrometer with an N$_2$ 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 an Xe lamp (Photon Technology
International) light through two monochromators (Acton, Princeton Instruments), and detected by an 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. Transient data were collected with 625 nm excitation with excitation intensity of 120 $\mu$J cm$^{-2}$ 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.

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 an N$_2$ 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, an Si photodiode-based detection system (Costronics Electronics, probe wavelength range: 400-1,100 nm, time resolution: ~700 ns), and a TDS-2022 Tektronix oscilloscope. Monochromatic probe light was obtained from the halogen lamp through two monochromators (JASCO, M10). Transient data were collected with the excitation intensity of 120 $\mu$J/cm$^2$ 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 an N$_2$ 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, probe wavelength range: 900-
2,500 nm, time resolution: ~150 ns), and a TDS-3012B Tektronix oscilloscope. 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.

**Analysis of transient emission data and charge injection yield.** Transient photoluminescence decay data were analysed following the previously reported method. Briefly, the analysis was conducted using a rate equation including a first order recombination via carrier trap states, second order non geminate free charge carrier (electron and hole) recombination and charge transfer processes, as shown in Equation 1.

\[
- \frac{dn}{dt} = k_1 n + k_2 n^2 + k_e n + k_h n
\]  

(1)

where \( n \) is the photo-excited charge carrier density, \( k_1 \) is the rate constant of trap state mediated recombination, \( k_2 \) is the rate constant of electron-hole recombination, \( k_e \) is the injection rate of the electron from perovskite to TiO₂ conduction bands, \( k_h \) is the injection rate of the hole from a perovskite valence band to OMeTAD, and \( t \) is the time. Here, we do not include three body Auger recombination, since the excitation intensity is relatively low (0.01-50 μJ cm⁻²).

Solving Equation 1 provides,
For analysis of the perovskite excited state, i.e., data for glass/MA$_3$PbI$_3$ and Al$_2$O$_3$/MA$_3$PbI$_3$,

Equation 1 is simplified to,$^{[12]}$

\[
\frac{d}{dt}n = k_1n + k_2n^2
\]  

(3)

Solving Equation 3 provides,

\[
n(t) = \frac{k_2n_0}{k_1 \exp(k_1t) - k_2n_0 + k_2n_0 \exp(k_1t)}
\]  

(4)

where \(n_0\) is the initial amplitude, i.e. at \(t = 0\).

For analysis of the electron injection dynamics, i.e. data for FTO/c-TiO$_2$/MA$_3$PbI$_3$ and FTO/c-TiO$_2$/p-TiO$_2$/MA$_3$PbI$_3$, Equation 1 is simplified to,

\[
\frac{d}{dt}n = k_1n + k_2n^2 + k_e n
\]  

(5)

Solving Equation 5 provides,

\[
n(t) = \frac{(k_1 + k_e)n_0}{k_1 \exp(k_1t + k_e t) - k_2n_0 + k_2n_0 \exp(k_1t + k_e t) + k_e \exp(k_1t + k_e t)}
\]  

(6)
For analysis of the hole injection dynamics, *i.e.* data for glass/MA\textsubscript{PbI\textsubscript{3}}/OMeTAD or \textsubscript{Al}\textsubscript{2}O\textsubscript{3}/MA\textsubscript{PbI\textsubscript{3}}/OMeTAD, Equation 1 is simplified to,

\[
-\frac{dn}{dt} = k_1 n + k_2 n^2 + k_h n
\]  

(7)

Solving Equation 7 provides,

\[
n(t) = \frac{(k_1 + k_h)n_0}{k_1 \exp(k_1 t + k_h t) - k_2 n_0 + k_2 n_0 \exp(k_1 t + k_h t) + k_h \exp(k_1 t + k_h t)}
\]  

(8)

For all transient emission decays, global analysis was conducted.\(^{[12]}\)

Charge injection yields were estimated by comparing lifetimes of the observed photoluminescence decays. Since the excited state decay has two components, *i.e.* first and second order components, it is not simple to evaluate the lifetime. Here, we define an effective lifetime, \(\tau_{1/e}\),\(^{[12]}\)

\[
I_{PL}(\tau_{1/e}) = I_{PL}(0) / e
\]  

(9)

where \(I_{PL}(\tau_{1/e})\) is the intensity of photoluminescence at time \(\tau\) after the excitation. Charge injection yields were evaluated using the following equations, and the electron and hole injection yield was estimated using Equation 8 and 10, respectively.

\[
1 / \tau_{MAPbI_3} = 1 / \tau_{1/e(MAPbI_3)}
\]  

(10)
\[ \frac{1}{\tau_{\text{TiO}_2}} = \frac{1}{\tau_{1/e(\text{MAPbI}_3)}} + \frac{1}{\tau_e} = \frac{1}{\tau_{1/e(\text{TiO}_2)}} \]  

(11)

\[ \Phi_e = \frac{\tau_{\text{TiO}_2}}{\tau_e} = 1 - \frac{\tau_{\text{TiO}_2}}{\tau_{\text{MAPbI}_3}} \]  

(12)

\[ \frac{1}{\tau_{\text{OMeTAD}}} = \frac{1}{\tau_{1/e(\text{MAPbI}_3)}} + \frac{1}{\tau_h} = \frac{1}{\tau_{1/e(\text{OMeTAD})}} \]  

(13)

\[ \Phi_h = \frac{\tau_{\text{OMeTAD}}}{\tau_h} = 1 - \frac{\tau_{\text{OMeTAD}}}{\tau_{\text{MAPbI}_3}} \]  

(14)

where \( \tau_{\text{MAPbI}_3} \) is the lifetime of the observed photoluminescence decay for glass/\( \text{MAPbI}_3 \) or \( \text{Al}_2\text{O}_3/\text{MAPbI}_3 \), \( \tau_{\text{TiO}_2} \) is the lifetime of the observed photoluminescence decay for FTO/c-\( \text{TiO}_2 \)/\( \text{MAPbI}_3 \) and FTO/c-\( \text{TiO}_2 \)/p-\( \text{TiO}_2 \)/\( \text{MAPbI}_3 \), \( \tau_{\text{OMeTAD}} \) is the lifetime of the observed photoluminescence decay for glass/\( \text{MAPbI}_3 \)/OMeTAD or \( \text{Al}_2\text{O}_3/\text{MAPbI}_3 \)/OMeTAD, \( \tau_{\text{e-inj}} \) is the electron injection rate, \( \tau_{\text{h-inj}} \) is the hole injection rate, \( \Phi_e \) is the electron injection yield, and \( \Phi_h \) is the hole injection yield.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author. Photoluminescence spectra of \( \text{Al}_2\text{O}_3/\text{MAPbI}_3 \) and a porous TiO\(_2\) film (150 nm) with two different MAPbI\(_3\) thickness. Photoluminescence spectra of \( \text{Al}_2\text{O}_3/\text{MAPbI}_3 \) and FTO/c-\( \text{TiO}_2 \)/thin m-\( \text{TiO}_2 \) (150 nm)/MAPbI\(_3\)/OMeTAD and FTO/c-\( \text{TiO}_2 \)/thick m-\( \text{TiO}_2 \) (2.8 \( \mu \)m)/MAPbI\(_3\)/OMeTAD. Comparison of effective lifetimes obtained for glass/\( \text{MAPbI}_3 \), FTO/c-\( \text{TiO}_2 \)/thin m-\( \text{TiO}_2 \) (150 nm)/MAPbI\(_3\) and FTO/c-\( \text{TiO}_2 \)/thick m-\( \text{TiO}_2 \) (2.8 \( \mu \)m)/MAPbI\(_3\).

**Acknowledgements**

We acknowledge Prof. Kazunari Matsuda, Kyoto University, for SEM measurements. This work was supported by the JST PRESTO, Japan.
References


Scheme 5.1. Schematic diagrams of lead iodide perovskite solar cell structures. (a) mesoporous structure and (b) planar heterojunction structure. (c) Scheme showing photo-induced charge transfer process. In this study, mesoporous TiO$_2$ film thickness ($d_{m\text{-TiO}_2}$) and perovskite layer thickness ($d_{\text{perovskite}}$) will be altered to see their influence on photo-induced charge separation and recombination dynamics. $\tau_{\text{inj}}$ and $\tau_{\text{re}}$ represents photo-induced charge injection rate and charge recombination rate, respectively.
Figure 5.1. (a) Absorption spectra of FTO/c-TiO$_2$/MAPbI$_3$ and FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$.  
(b) Transient emission decays at 770 nm, obtained for glass/MAPbI$_3$, FTO/MAPbI$_3$ and FTO/c-TiO$_2$/MAPbI$_3$ with 405 nm excitation and excitation intensity of 0.1 μJ cm$^{-2}$. The black solid line shows results of fitting with Equation 3 and Equation 4.  
(c) Transient emission decays at 770 nm, obtained for glass/MAPbI$_3$, FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$ and FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$/OMeTAD with 405 nm excitation and excitation intensity of 0.1 μJ cm$^{-2}$. The black solid line shows results of fitting with Equation 3 and Equation 4.  
(d) Light intensity dependence on charge injection yields obtained for FTO/c-TiO$_2$/MAPbI$_3$, FTO/c-
TiO$_2$/m-TiO$_2$/MAPbI$_3$ and FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$/OMeTAD. The dotted line for each data set is shown as a guide.

![Absorption spectra](chart)

**Figure 5.2.** (a) Absorption spectra of perovskite/thin mesoporous TiO$_2$ film (m-TiO$_2$ thickness: ~150 nm) prepared by altering PbI$_2$ precursor concentration from 0.2 M to 1.1 M for the perovskite formation. (b) Surface SEM image of a perovskite layer on mesoporous TiO$_2$ films prepared with low and high concentrations of PbI$_2$ precursors: 0.2 M (top) and 1.1 M (bottom). (c) Cross-sectional SEM image of a FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$/OMeTAD film prepared with PbI$_2$ concentration of 1.1 M.
Figure 5.3. (a) Transient absorption spectra of m-TiO₂/MAPbI₃ films covered with and without OMeTAD, obtained at 2 µs after 625 nm excitation with excitation intensity of 120 μJ cm⁻². The dotted line indicates an OMeTAD oxidized state spectrum obtained by chemically oxidizing OMeTAD. (b) Transient absorption growth of m-TiO₂/MAPbI₃ films covered with OMeTAD, monitored at 500 nm.
Figure 5.4. (a) Transient emission decays at 770 nm, obtained for a porous TiO₂ film with various MAPbI₃ thickness after 625 nm excitation with excitation intensity of 0.1 μJ cm⁻². The number indicates PbI₂ concentration used to prepare the perovskite layer. The black solid line shows results of fitting using Equation 6. Excited state decay obtained for glass/MAPbI₃ (prepared with 1.1 M PbI₂) under the same excitation condition is also shown as reference. (b) Transient absorption decays monitored at 1,600 nm, for a porous TiO₂ film with various MAPbI₃ thickness and with OMeTAD after 625 nm excitation with excitation intensity of 120 μJ cm⁻². The black solid line indicates results from the stretched exponential fitting. (c)
Perovskite thickness dependence of charge injection yield (electron and hole) and charge recombination lifetimes. The dotted line for each data set is shown as a guide.

**Figure 5.5.** (a) Transient emission decays at 770 nm, obtained for glass/MAPbI$_3$, FTO/c-TiO$_2$/thin m-TiO$_2$ (150 nm)/MAPbI$_3$ and FTO/c-TiO$_2$/thick m-TiO$_2$ (2.8 μm)/MAPbI$_3$ with 625 nm excitation and excitation intensity of 0.5 μJ cm$^{-2}$. PbI$_2$ concentration is 0.2 M to deposit a perovskite film inside and on top of the porous TiO$_2$ layer. The black solid line shows results of fitting with Equation 3. (b) Light intensity dependence on electron injection yields obtained for FTO/c-TiO$_2$/thin m-TiO$_2$ (150 nm)/MAPbI$_3$ and FTO/c-TiO$_2$/thick m-TiO$_2$.
(2.8 μm)/MAPbI₃. The dotted line for each data set is shown as a guide. (c) Transient absorption decays monitored at 1,600 nm, for FTO/c-TiO₂/thin m-TiO₂ (150 nm)/MAPbI₃/OMeTAD and FTO/c-TiO₂/thick m-TiO₂ (2.8 μm)/MAPbI₃/OMeTAD after 625 nm excitation with excitation intensity of 120 μJ cm⁻². The black solid line indicates results from the stretched exponential fitting. (d) m-TiO₂ film thickness dependence of charge injection yield (electron and hole) and charge recombination lifetimes. The charge injection yields were estimated with photoluminescence decay lifetimes with the excitation intensity of 10 nJ/cm². The dotted line for each data set is shown as a guide.

Table 5.1. Summary of charge (electron and hole) injection yield and charge recombination dynamic data.

<table>
<thead>
<tr>
<th>n_{perovskite} / nm</th>
<th>d_{m-TiO₂} / nm</th>
<th>Electron injection yield / %</th>
<th>Hole injection yield / %</th>
<th>Charge recombination lifetime / ms</th>
<th>Stretched parameter α</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>150</td>
<td>96.7 ± 1.2</td>
<td>95.1 ± 1.8</td>
<td>0.74</td>
<td>0.44</td>
</tr>
<tr>
<td>200</td>
<td>150</td>
<td>91.9 ± 2.4</td>
<td>95.2 ± 1.5</td>
<td>0.53</td>
<td>0.31</td>
</tr>
<tr>
<td>280</td>
<td>150</td>
<td>86.4 ± 2.9</td>
<td>96.5 ± 1.2</td>
<td>6.28</td>
<td>0.31</td>
</tr>
<tr>
<td>300</td>
<td>150</td>
<td>81.2 ± 3.5</td>
<td>98.3 ± 1.0</td>
<td>42.2</td>
<td>0.51</td>
</tr>
</tbody>
</table>
Optimization of mesoscopic CH$_3$NH$_3$PbI$_3$ perovskite cell structure through the study of thickness controlling interfacial charge transfer dynamics

Maning Liu, Masaru Endo, Hidetaka Nishimura, Atsushi Wakamiya, and Yasuhiro Tachibana*

**Figure S5.1.** (a) Photoluminescence spectra of Al$_2$O$_3$/MAPbI$_3$ and a porous TiO$_2$ film (150 nm) with two different MAPbI$_3$ thickness (prepared with 0.2 or 1.1 M PbI$_2$ concentration to control perovskite thickness) and with OMeTAD after 625 nm excitation. (b) Photoluminescence spectra of Al$_2$O$_3$/MAPbI$_3$ and FTO/c-TiO$_2$/thin m-TiO$_2$ (150 nm)/MAPbI$_3$/OMeTAD and FTO/c-TiO$_2$/thick m-TiO$_2$ (2.8 μm)/MAPbI$_3$/OMeTAD with 625 nm excitation. The photoluminescence spectra were normalized with the number of absorbed photons at the excitation wavelength and to the Al$_2$O$_3$/MAPbI$_3$ emission amplitude at a peak wavelength.
Figure S5.2. Comparison of effective lifetimes obtained for glass/MAPbI$_3$, FTO/c-TiO$_2$/thin m-TiO$_2$ (150 nm)/MAPbI$_3$ and FTO/c-TiO$_2$/thick m-TiO$_2$ (2.8 μm)/MAPbI$_3$ with 625 nm excitation.
Chapter 6 Potential Level Dependent Interfacial Charge-Carrier Dynamics in a \( \text{CH}_3\text{NH}_3\text{PbI}_3 \)-based Perovskite Film

Introduction

Rapid development of solid-state photovoltaics has been promoted based on \textit{organic-inorganic} trihalide perovskite employed as the light absorber in the device. Generally, the \textit{organic-inorganic} trihalide perovskite shows excellent optical property in high absorbance of a wide light spectrum,\(^1\) and promising electronic properties in extremely long charge carrier diffusion length (more than 1 \( \mu \text{m} \))\(^2\) and long-lived \textit{charge carrier} lifetime in excited state (several hundreds of nanoseconds).\(^3\) It have been reported that the interfacial charge carrier transfer dynamics between \textit{organic-inorganic} trihalide perovskite and charge selective layers (CSLs) have a significant impact on the final performance of solar cells.\(^4\)\(^-\)\(^5\) Several key parameters intensively influence the charge transfer dynamics at the perovskite interfaces. In Chapter 5, it is demonstrated that the charge separation and charge recombination kinetics are dependent on excitation intensity\(^6\) and thicknesses of perovskite and mesoporous \( \text{TiO}_2 \) (mp-\( \text{TiO}_2 \)) layers. It has been found that overall high charge separation efficiency (\( \sim 100\% \)) with prolonged charge separated state lifetime can be typically obtained when utilizing thick perovskite layer (ca. 300 nm) and medium thick mp-\( \text{TiO}_2 \) layer (ca. 500~600 nm) upon weak excitation intensity (\(< 50 \text{ nJ cm}^{-2} \)). However, the further investigation on the potential levels,
i.e. conduction (CB) and valence band (VB), of perovskite and CSLs controlling the interfacial charge transfer dynamics is still limited by reviewing the previous literatures.

In this chapter, by tuning the potential levels of perovskite and CSLs (electron and hole selective layers) separately through a series of approaches including adjustable excitation wavelength, external bias application and involvement of dopants, I have systematically investigated the potential level dependent charge carrier transfer dynamics for a MAPbI$_3$-based film (mp-TiO$_2$/perovskite/OMeTAD). The electron injection rate was accelerated by enhancing the excitation photon energy (lower the wavelength), due to the hot electron generated by strong excitation energy can be injected from top of perovskite CB into TiO$_2$ CB, which is much swifter than the injection rate of the cool electron generated at the bottom of perovskite CB by weak excitation energy. The tunable CB of TiO$_2$ upon applied negative bias proved that the smaller gap between perovskite CB and TiO$_2$ CB facilitates the efficient electron injection. With doping additives in OMeTAD, the HOMO level of OMeTAD shifted towards more negative direction, resulting in prolonged charge recombination lifetime between an electron in TiO$_2$ CB and a hole at HOMO level of OMeTAD.

References


Potential Level Dependent Interfacial Charge-Carrier Dynamics in a CH$_3$NH$_3$PbI$_3$-based Perovskite Film

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ABSTRACT

Organic-inorganic halide-based perovskite solar cells (PSCs) have recently attracted unprecedented increasing attentions due to their unexpected high efficiency (the record power conversion efficiency has been announced to be over 22%) and low cost manufacturing. It has been thought that the high efficiency was mainly ascribed to the abundant optical absorption over a wide range (up to 800 nm), the long lifetimes of charge excitons (in the order of 10 ns ~ a few 100 ns), and the long diffusion lengths of charge carriers (more than 1 μm) of the perovskite absorbers. However, much of the fundamental photoinduced properties of perovskite relating to the high performance of PSCs are remained to be probed. The interfacial charge transfer dynamics, i.e. charge separation and recombination processes, are crucial for photovoltaic performances. We previously reported excitation intensity dependent perovskite excited state lifetime (5~180 ns) and charge separation (electron and hole injection) at the perovskite interfaces. In this study, we systematically investigated the potential level dependent charge separation and charge recombination dynamics of CH$_3$NH$_3$PbI$_3$-based films by employing TiO$_2$ nanopores as the electron transfer materials (ETM) and spiro-OMeTAD as the hole transfer material (HTM). We clarified the dual valence band (VB) model induced by strong excitation energy (low wavelength), resulting in the accelerated electron injection rate while remaining the swift hole injection rate. In addition, the conduction band (CB) level of TiO$_2$ tuned by external application of negative bias was also proved to make impact on electron injection kinetics. It was found that the doped OMeTAD with more negative HOMO level can effectively suppress the charge recombination, indicating a critical nature to improve the performance of PSCs.
**KEYWORDS**: potential level, interfacial charge-carrier transfer dynamics, MAPbI$_3$-based perovskite film, excitation wavelength, bias application, doped OMeTAD.
Over the last few years, organic-inorganic trihalide perovskite solar cells (PSCs) have been widely investigated as one of the most promising candidates for photon-to-electron conversion. \cite{1} PSCs possess several outstanding merits including excellent electronic properties, tunable bandgap, splendid charge transport abilities, and facile low-cost processing techniques. \cite{2} Perovskite photovoltaics have presented unparalleled progress in power conversion efficiency (PCE) in the recent 3-4 years, dramatically increasing up to date 22.1\%, \cite{3} showing aggressive competitiveness with other new generation solar cells even with conventional silicon solar cells.

In terms of previous extensive researches, the state-of-the-art PSCs have been constantly developed by employing several advanced device engineering strategies such as solvent engineering, \cite{4} interfacial engineering \cite{5} and bandgap engineering. \cite{6} Although those engineering methods can effectively improve the performance of perovskite devices, the understanding of the underlying mechanism of high-performance perovskite-based solar cells is still restricted, including conditions influencing photoexcited charge carrier dynamics, charge separation and charge recombination in PSCs. We previously proved photoexcitation intensity dependent charge carriers (electron and hole) separation dynamics \cite{7} for m-TiO$_2$/MAPbI$_3$/OMeTAD film in mesoscopic structure by clarifying electron injection rate of \(~11\) ns and hole injection rate of \(~1.8\) ns, which are much slower than some reported utilizing femtosecond transient absorption spectroscopies (from 200 fs to several tens of picoseconds). \cite{8} We attributed those differences to be likely in the various excitation energies (wavelengths) or multi-phasic electron injection processes like more than 3 components covering fs-ns time scales. Eric’s group \cite{9} reported a very slow hole injection rate \(~5\) ns at the perovskite/NiO interface upon low excitation wavelength at 450 nm. They also demonstrated a composite consecutive kinetic model revealing a transition for high excitation energy generated excitons (hot electrons
and holes) involving hot-hole cooling from valence band (VB) 2 to VB1 and hot-electron relaxation in conduction band (CB) in perovskites, and surface-state (SS) excitonic relaxation from CB to SS. Douhal’s group [10] investigated excitation energy dependent charge separation dynamics for m-TiO$_2$/MAPbI$_3$/OMeTAD film, presenting a dual VB model with ultrafast electron (< 200 fs) and hole (~ 0.7 ps) injection rates upon strong excitation energy at 460 nm and no charge injection upon weak excitation energy at 750 nm. However, on the basis of previous reported charge transfer dynamics related to the conditions influencing potential levels (CB and VB) of perovskites and charge selective layers, *i.e.* electron (ETM) and hole (HTM) transfer materials, the comprehensive study of the charge separation and recombination dynamics at the ETM/perovskites/HTM interfaces is still poor.

In this letter, by employing a series of transient absorption and emission spectroscopies, we have systematically and quantitatively investigated the potential level dependent charge transfer dynamics, *i.e.* charge injection and charge recombination processes, at the interfaces of MAPbI$_3$-based perovskites and charge selective layers including mesoporous TiO$_2$ as ETM and spiro-OMeTAD as HTM. Several approaches have been employed to tune the potential levels for perovskites and charge selective layers. By altering the excitation energy (wavelength) the generated excitons can transit between different valence bands in perovskites for charge transfer. Bias application method has been used to change the conduction band level of TiO$_2$, resulting in reversible electron injection between CB of perovskite and CB of TiO$_2$. In addition, additives doping method has been utilized to modify the valence band (or HOMO) level of OMeTAD towards more negative direction, leading to extended charge recombination lifetime compared to the one with no dopant.
To determine the dependence of perovskite potential levels on the interfacial charge transfer dynamics, three samples have been employed, including glass/MAPbI₃, FTO/c-TiO₂/m-TiO₂/MAPbI₃ and FTO/c-TiO₂/m-TiO₂/MAPbI₃/OMeTAD. Figure 6.1a shows the comparison of absorption spectra obtained from above samples. They are similar to those reported in the literature showing a spectral shape with a shoulder around 750 nm, and no significant difference is observed between the three spectra, indicating that they result from similar band-to-band transitions in the perovskite layer. The entire UV and visible light can be absorbed by perovskite layer. To realize the control of perovskite potential levels for the dynamic study, i.e. transition of CB and VB, we utilized various excitation wavelengths to excite MAPbI₃ layer for transient emission and absorption measurements. Figure S6.1a shows the excitation wavelength dependent transient emission decays for glass/MAPbI₃, monitored at 770 nm with excitation intensity of 0.1 μJ cm⁻². Since the glass is an insulator, the data indicate that the perovskite excited state decays. Interestingly, the excited state lifetime is likely independent on the excitation wavelength. All decays were well fitted by a reported rate
Figure 6.1. (a) Absorption spectra of glass/MAPbI₃, FTO/c-TiO₂/m-TiO₂/MAPbI₃ and FTO/c-TiO₂/m-TiO₂/MAPbI₃/OMeTAD. (b) Transient emission decays at 770 nm, obtained for FTO/c-TiO₂/m-TiO₂/MAPbI₃ with various excitations at excitation intensity of 0.01 μJ cm⁻². The black solid line shows results of fitting with a rate equation. (c) Transient emission decays at 770 nm, obtained for FTO/c-TiO₂/m-TiO₂/MAPbI₃/OMeTAD with various excitations at excitation intensity of 0.01 μJ cm⁻². The black solid line shows results of fitting with a rate equation.
equation \[7\], implying that non-geminate electron-hole recombination occurs within a perovskite layer. \[8b, 11\] In addition to the excited state decays obtained at excitation intensity of 0.1 \(\mu\)J cm\(^{-2}\), we have applied a wide range of excitation intensity in four orders upon various excitation wavelengths. To simplify the evaluation of transient emission decays, we employ a reported definition of an effective lifetime, \(\tau_{1/e}\). The excitation intensity dependent excited state effective lifetimes upon different excitation wavelengths are shown in Figure S6.1b. The decrease of effective lifetimes with the increase of excitation intensity is consistent with our previous report \[7\] and a similar effective lifetime at particular excitation intensity has been observed although the excitation wavelength varies. It is known that shorter excitation wavelength such as 405 nm or 480 nm for our case possesses relatively strong photon energy, which potentially can invoke a transition from the bottom of valence band (VB2) to generate hot excitons in the conduction band (CB) of perovskite. Therefore, this model is defined as a two valence band model. \[10, 12\] On contrast, longer excitation wavelength such as 735 nm that is close to the absorption band edge of perovskite, generally obtains weak photon energy that can only generate cool excitons from the top of valence band (VB1) to the bottom of CB. However, based on our observation for the decay kinetics of perovskite excited state, the relaxation lifetime remains similar independently on incident photon energy, indicating that the transition time from hot excitons to cool excitons is ultrafast in picosecond timescale \[10\] compared to the transient emission decay lifetime from CB to VB1 in nanosecond timescale once the excitons are generated (see Scheme 6.1).

In our previous report, we have proved that mesoporous TiO\(_2\) nanopores are more favorable for the efficient electron injection from perovskite excited state to TiO\(_2\) conduction band
Table 6.1. Summary of charge (electron and hole) injection yield and charge recombination dynamic data by the dependence of excitation wavelength.

<table>
<thead>
<tr>
<th>Excitation wavelength / nm</th>
<th>Electron injection rate / ns</th>
<th>Electron injection yield / %</th>
<th>Hole injection yield / %</th>
<th>Charge recombination lifetime / ms</th>
<th>Stretched parameter α</th>
</tr>
</thead>
<tbody>
<tr>
<td>405</td>
<td>4.1</td>
<td>88.5%</td>
<td>99.2%</td>
<td>26.5</td>
<td>0.48</td>
</tr>
<tr>
<td>480</td>
<td>22.7</td>
<td>85.5%</td>
<td>99.0%</td>
<td>30.1</td>
<td>0.52</td>
</tr>
<tr>
<td>550</td>
<td>27.8</td>
<td>84.6%</td>
<td>98.5%</td>
<td>5.3</td>
<td>0.53</td>
</tr>
<tr>
<td>625</td>
<td>31</td>
<td>81.8%</td>
<td>98.3%</td>
<td>49.3</td>
<td>0.70</td>
</tr>
<tr>
<td>735</td>
<td>93</td>
<td>64.1%</td>
<td>98.1%</td>
<td>1310</td>
<td>0.84</td>
</tr>
</tbody>
</table>

compared to planar heterojunction such as compact TiO$_2$ layer. Figure 6.1b presents a comparison of transient emission decays for FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$ film with the representative excited state decay (405 nm excitation), excited at various excitation wavelengths upon excitation intensity of 0.01 μJ cm$^{-2}$. Clearly, the decay has been accelerated by shortening excitation wavelength, owing to the faster electron injection rate. The electron injection rate has been estimated depending on fitted effective lifetimes of transient emission decays with detailed calculation method described in experimental section. The summary of evaluated electron injection rates by the dependence of excitation wavelength has been shown in Table 6.1. The electron injection rate has been largely extended from 4.1 ns excited at 405 nm to 93 ns excited at 735 nm. Such case suggests that hot electrons generated upon high photon excitation energy are quicker to be injected from the top of CB in perovskite into TiO$_2$ CB, rather than relatively slower injection for cool electrons from the bottom of CB in perovskite into TiO$_2$ CB (see Scheme 6.1). One possible reason is that the surface states most likely exist on the bottom of CB in perovskite, which tend to trap the cool electrons for the further injection into the electron selective layer. Be noted that the absorbance of perovskite layers at shorter wavelengths is much
higher than that at longer wavelengths, suggesting that higher charge carrier density would be potentially formed at the TiO$_2$ interface under the shorter wavelength excitations, which probably causes rapid bimolecular recombination decay as one factor. Moreover, the excitation wavelength dependent transient emission decays for FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$/OMeTAD film were measured to assess hole injection process compared to the excited state decay and are shown in Figure 6.1c. All decays indicate similar accelerations compared to the ones obtained from the perovskite film without OMeTAD (shown in Figure 6.1b) whatever excitation wavelength is applied, meaning that ultrafast hole injection from perovskite VB (VB1 or VB2) to OMeTAD VB occurs that is almost nonsensitive to the excitation photon energy as long as the excitons are generated. To quantitatively evaluate charge carrier injection kinetics, we employ a reported analysis method$^{19}$ to calculate the charge carrier (electron and hole) injection yield based on the fitted effective lifetimes of transient emission decays upon perovskite excited state and charge extraction state. Figure 6.2b shows estimated charge carrier injection yield as a function of excitation wavelength, obtained at weak excitation intensity of 0.01 µJ cm$^{-2}$. A moderate decrease of electron injection yield with the increase of excitation wavelength has been observed, consistent with faster electron injection rate obtained from strong photo-excitation energy. In contrast, a constantly extreme high hole injection yield (~100%) has been noted over the whole range of excitation wavelength, indicating that efficient hole injection is mainly determined by the addition of OMeTAD and much less sensitive with incident photon energy. The excitation dependent charge carrier yields (electron and hole) are summarized in Table 6.1.

Furthermore, we turn to assess the excitation photon energy influencing charge separated state and recombination dynamics monitored by Vis-NIR transient absorption (TA) spectroscopy. TA spectra at 2 µs after various excitations for FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$/OMeTAD are shown in
Figure 6.2a. The residual emission of the excited state was observed at 700-900 nm, which is similar to our previous report. The enhanced negative amplitude with the increase of excitation wavelength may attribute to the slight decrease of hole injection yield mentioned above with the

![Figure 6.2a](image1.png)

Figure 6.2. (a) Transient absorption spectra of m-TiO$_2$/MAPbI$_3$/OMeTAD film, obtained at 2 μs after various excitations with excitation intensity of 120 μJ cm$^{-2}$. (b) Charge injection yields
electron and hole injections) obtained for FTO/c-TiO₂/m-TiO₂/MAPbI₃ and FTO/c-TiO₂/m-TiO₂/MAPbI₃/OMeTAD, as a function of excitation wavelength at excitation intensity of 0.01 μJ cm⁻². The dotted line for each data set is shown as a guide. (c) Normalized transient absorption decays monitored at 1,600 nm, for m-TiO₂/MAPbI₃/OMeTAD film after various excitations with excitation intensity of 120 μJ cm⁻². The solid line indicates results from the stretched exponential fitting. The relative amplitude of each decay is divided by the amplitude of decay upon 405 nm excitation.

increase of excitation wavelength. The positive amplitudes with a peak at around 1600 nm were noted, and are consistent with previous observation, which has been assigned to the OMeTAD oxidized state. Since the applied excitation intensity was as high as 120 μJ cm⁻², the maximum hole injection yield should be less than 50% based on our previous study of excitation intensity dependent charge injection yield. The slight difference between the TA peaks at 1600 nm obtained upon different excitation wavelengths, likely due to the lower incident photon energy from longer wavelength can further reduce the hole injection yield, which is consistent with the previous observation for transient emission decays. Charge recombination dynamics by the dependence of excitation wavelength were monitored for FTO/c-TiO₂/m-TiO₂/MAPbI₃/OMeTAD. The OMeTAD oxidized state decays probed at 1600 nm have been presented in Figure 6.2c. In all cases, the reactions occur at least after 10 μs by following the kinetics behavior of stretched exponential decay. The well fitted results for all TA decays have been summarized in Table 6.1. Surprisingly, the TA decay excited at 735 nm exhibits an extremely long-lived lifetime compared to other decays excited by shorter wavelengths, which we believe has not been observed in previous literature. The underlying reason to explain this
long charge recombination lifetime at longer wavelength excitation is still not fully clear. One possible reason is that by lowering the excitation photon energy (towards long wavelength) the number of injected charge carriers (holes) turns smaller, which can be identified by weakened amplitude of transient absorption decay upon longer wavelength, therefore, the excited charge intensity decreases with the increase of excitation wavelength, resulting in slow charge recombination dynamics.

Figure 6.3. (a) Applied bias dependent transient emission decays monitored at 770 nm for MAPbI₃-based perovskite device (FTO/c-TiO₂/m-TiO₂/MAPbI₃/OMeTAD/Au), obtained at 625 nm excitation with excitation intensity of 0.04 μJ cm⁻². The bias was applied from 0 V to -2.1 V with -0.1 V step. Inset shows the comparison of perovskite excited state decay for glass/MAPbI₃ with no bias application and one transient emission decay for perovskite device applied at 0 V. Inset shows the comparison of excited state decay with no bias application obtained from glass/MAPbI₃ and one transient emission decay upon 0 V bias as a representative. (b) Transient
emission intensity peaks (red dots) and corresponding effective lifetimes (green dots) as a function of applied bias on device, obtained at 625 nm excitation with excitation intensity of 0.04 μJ cm\(^{-2}\).

We now turn to the assessment of charge transfer dynamics influenced by tuning the potential level of charge selective materials, \(i.e.\) CB of TiO\(_2\) and HOMO level of OMeTAD. For the former case, we employ the electrochemical method\([13]\) in which a bias is applied on the perovskite cell (FTO/c-TiO\(_2\)/m-TiO\(_2\)/MAPbI\(_3\)/OMeTAD/Au) by connecting a potentiostat to FTO as working electrode and gold as reference and counter combined electrode, respectively. It is known that the negative bias application can alter the CB of nanocrystalline TiO\(_2\) which has been popularly utilized in polymer hybrid solar cells.\([13]\) Applied bias dependent transient emission decays for FTO/c-TiO\(_2\)/m-TiO\(_2\)/MAPbI\(_3\)/OMeTAD/Au were measured after 625 nm excitation with a weak excitation intensity of 0.04 μJ cm\(^{-2}\), and are shown in Figure 6.3a. Inset shows the comparison of the excited state decay with no bias application obtained from glass/MAPbI\(_3\) and one transient emission decay upon 0 V bias as a representative. A huge quenching of transient emission amplitude has been observed, indicating that the charge injection (electron and hole) occurs efficiently with and without bias application, consistent with the high charge injection yield (\(\sim\) 99\%) can be obtained upon weak excitation intensity (\(<\) 50 nJ cm\(^{-2}\)).\(^{19}\) We extracted the emission peaks and effective lifetimes for all decays (except excited state decay) as a function of applied bias and plotted in Figure 6.3b. A similar trend has been observed for both emission peaks and effective lifetimes by applying bias from 0 V to -2.1 V. It is noted that the emission amplitude was slightly quenched decreasing up to the applied bias of -0.9 V, meaning that the initial rising of TiO\(_2\) CB can still facilitate electron injection from perovskite
CB to TiO₂ CB (see Scheme 6.1) since the excitation intensity was 40 nJ cm⁻² and the estimated electron injection yield was around 90% [⁷] without any bias application. The reduced effective lifetime up to -0.9 V bias also reveals that the accelerated electron injection rate was obtained by increasing the CB of TiO₂ to match the CB of perovskite as more favorable cascade structure for the potential level engineering. However, with the further negative bias application, the emission amplitude exhibited continuous increasing by applying more negative bias up to -2.1 V. Since the applied negative bias was against OMeTAD to tune the CB of TiO₂, more and more electrons accumulated on the CB of TiO₂ while keeping to raise the level of TiO₂ CB until achieving the same level of perovskite CB, resulting in no electron injection from perovskite CB to TiO₂ CB. Afterwards, the accumulated electrons on TiO₂ CB can rather inject to perovskite CB, showing more emissive signals upon relaxation to perovskite VB1. The extended effective lifetime after applying -1.2 V bias also confirmed the retarding of electron injection rate from perovskite CB to TiO₂ CB owing to the equal or higher conduction band level of TiO₂ under bias compared to perovskite. This study of bias dependent transient emission dynamics for MAPbI₃-based perovskite device supplies hints for potential level engineering particularly on the conduction band of electron transfer material (HTM). Compared to current TiO₂ nanopores as ETM, there is still some space to improve electron injection kinetics once the CB of ETM can be slightly increased towards perovskite CB, such as ZnO nanopores or PCBM for planar heterojunction structure.
Figure 6.4. (a) Transient absorption spectrum for m-TiO$_2$/MAPbI$_3$/OMeTAD without (green line) and with (red line) dopants in OMeTAD, obtained at 2 μs delay after 625 nm excitation with excitation intensity of 120 μJ cm$^{-2}$. (b) Transient absorption decays monitored at 1600 nm for m-TiO$_2$/MAPbI$_3$/OMeTAD without (green dots) and with (red dots) dopants in OMeTAD. The solid line demonstrates a result of stretched exponential fitting.

It is well known that the application of spiro-OMeTAD as HTM in the fabrication of perovskite solar cell requests some additives, \[^{14}\] \textit{i.e.} lithium salt (Li-TFSI) and 4-\textit{tert}-butylpyridine (tBP), to enhance the hole doping of OMeTAD, resulting in the increased open circuit voltage and fill factor for cell performance improvement. Those additives have also been proved to play a role of a catalyst in the formation of oxidized OMeTAD via a photoinduced reaction. \[^{15}\] In addition, some new additive like cobalt salt (Co(III)-complex) has been employed to further increase the charge conductance, reducing the charge transport (hole) resistance of spiro-OMeTAD. \[^{16}\] Murata’s group reported one key factor for HTM such as spiro-OMeTAD to perform efficiently in perovskite solar cells is that the OMeTAD HOMO and LUMO levels
should be controlled at least 0.1 and 0.25 eV higher than the perovskite VB and CB, respectively. They also proved that with doped additives such as Co(III)-complex both of HOMO and LUMO levels of OMeTAD shift to more negative levels. To investigate the effect of those doped additives in spiro-OMeTAD on the charge transfer kinetics, we have assessed the charge separated state and recombination dynamics by comparing between the m-TiO₂/MAPbI₃/OMeTAD films with and without dopants. Figure 6.4a shows the TA spectra for the perovskite deposited OMeTAD films in the absence (neat film) and presence (doped film) of additives, monitored at 2 μs delay after excitation at 625 nm with the excitation intensity of 120 μJ cm⁻². Both films indicate nearly identical TA spectra in a wide range of Vis-NIR probe light. As the spectra have also been normalized with the number of absorbed photons at excitation wavelength for two films, clarifying that the charge separation process, i.e. electron and hole injections, is non-sensitive to the addition of dopants in OMeTAD. Charge recombination dynamics were observed for above two films and the OMeTAD oxidized state decays monitored at 1600 nm are presented in Figure 6.4b. The reaction in the m-TiO₂/MAPbI₃/OMeTAD without any dopants occurs in quite fast time scale (<150 ns, the instrument response) while the decay for the film with doped OMeTAD appears to start after 5 μs. This postponed reaction is surely due to the involvement of doped additives in OMeTAD, improving the hole conductivity and enhancing the hole transport. Both decays were satisfactorily fitted by stretched exponential function. Interestingly, the charge recombination between an electron in the TiO₂ conduction band and a hole at the OMeTAD with doped additives is roughly 26 times slower with a lifetime of 223 ms (stretched parameter α: 0.39) compared to the case without doped additives. We attributed this prolonged recombination lifetime to the more negative HOMO level of doped OMeTAD, leading to a larger band edge gap between an electron on TiO₂ CB and a hole at HOMO level of doped
OMeTAD (see Scheme 6.1). It is noteworthy that the reported HOMO level of Li-TFSI or Co(III)-complex is lower than that of OMeTAD, \(^{15-16}\) inducing a negatively shift in the Fermi level of OMeTAD to the HOMO level owing to the increased hole concentration, therefore, the gap between the quasi-Fermi level of TiO\(_2\) and the Fermi level of spiro-OMeTAD can be enlarged, assisting to strengthen a higher open circuit voltage as another factor.

Scheme 6.1 shows an overall mechanism of potential level dependent interfacial charge transfer dynamics in an m-TiO\(_2\)/MAPbI\(_3\)/OMeTAD film. The rate of electron injection from CB of perovskite into CB of TiO\(_2\) can be accelerated by increasing the excitation photon energy (lower the wavelength) while the swift hole injection rate is almost independent on the excitation energy. Initial negative bias application (up to –0.9 V) on CB of TiO\(_2\) can slightly promote electron injection rate, suggesting that the CB level of ETM can also influence the rate of electron injection from CB of perovskite into CB of ETM. Moreover, the yield of hole injection from VB of perovskite to HOMO level of OMeTAD is nonsensitive to the OMeTAD HOMO level controlled by dopants, however, the VB level of OMeTAD can significantly influence the charge recombination rate between an electron on CB of TiO\(_2\) and a hole at HOMO of OMeTAD, indicating retarded charge recombination dynamics with negatively shifted HOMO level of OMeTAD by doping additives such as Co(III)-complex in OMeTAD.
Scheme 6.1. A mechanism diagram showing the studied transitions for the related processes in a m-TiO$_2$/MAPbI$_3$/OMeTAD film, influenced by the various potential levels for perovskite and charge selective materials. CB: conduction band; VB: valence band; SS: surface state.

In conclusion, we have identified that excitation intensity dependent excited state lifetime is almost independent on the excitation photon energy, owing to relatively long relaxation time (in tens of nanoseconds scale) from CB of perovskite to VB of perovskite for both hot (high photon energy) and cool (low photon energy) carriers, compared to negligible ultra-fast transition rate (in < 1 ps scale)\textsuperscript{[10]} for hot carriers cooling to CB of perovskite. Nevertheless, the electron injection kinetics show accelerate injection rate from CB of perovskite into CB of TiO$_2$ with the increase of excitation photon energy by lowering the excitation wavelength, due to the hot electrons can be extracted more actively than the cool electrons which can potentially be trapped.
on surface state of perovskite CB. On contrary, both hot and cool holes can realize swift injection from VB of perovskite to HOMO of OMeTAD with nearly no influence from various excitation photon energies, mainly contributing to the high-performance of perovskite devices. Besides, both CB level of TiO$_2$ and HOMO level of OMeTAD can significantly influence the charge transfer dynamics at the perovskite interfaces. The electron injection rate can be fastened when CB level of ETM such as TiO$_2$ is more close to CB level of perovskite, resulting in optimum cascade of energy level to promote electron extraction. The charge separate state lifetime can be effectively prolonged by more negatively shifting HOMO level of HTM such as doped OMeTAD while remaining identical hole injection yield. Our study for potential level dependent charge transfer dynamics suggests that the tunability of potential levels for perovskites and charge selective layers is crucial to control the charge transfer kinetics at the perovskite interfaces, and the performance of PSCs is expected to be further improved once the potential levels of perovskite materials, ETM and HTM are kinetically optimized.
Experimental Methods

Materials. Dehydrated PbI$_2$ and CH$_3$NH$_3$I (MAI) powder were purchased from Tokyo Chemical Industry, CO., LTD. (TCI). 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, H$_2$O < 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(acetylacetonate) was purchased from Sigma-Aldrich Co. LLC. A nanocrystalline TiO$_2$ paste (PST-18NR, anatase, particle diameter: ca. 20 nm) for spin coating and screen printing was obtained from JGC C&C. Al$_2$O$_3$ powder (Aeroxide Alu C, particle diameter: approximately 13 nm) was provided by Evonik Degussa GmbH.

Sample preparation. CH$_3$NH$_3$PbI$_3$ perovskite layer was deposited on a various different substrate. The substrate includes a slide glass (glass/MAPbI$_3$), a fluorine doped tin oxide (FTO, 15 mm × 25 mm) glass (FTO/MAPbI$_3$), a compact TiO$_2$ layer prepared on FTO (FTO/c-TiO$_2$/MAPbI$_3$), or a nanocrystalline TiO$_2$ film with (FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$/OMeTAD) or without (FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$) OMeTAD. A compact TiO$_2$ layer (c-TiO$_2$) was deposited on a FTO substrate by spray pyrolysis of 0.05 M titanium di-isopropoxide bis(acetylacetonate) solution in ethanol at 450 ºC.$^{[18]}$

A transparent TiO$_2$ nanocrystalline film was prepared on the as-prepared compact TiO$_2$ layer or a slide glass. The film thickness was controlled by depositing with two different methods, spin coating and screen printing methods. A thin transparent TiO$_2$ nanocrystalline film (thickness: 200 nm) was deposited by spin coating at 5000 rpm for 30 s using an ethanol suspension of TiO$_2$
paste (TiO\(_2\) paste:ethanol = 1:3.5 wt. ratio). The film thickness was measured by a surface profiler (KLA-Tencor P-16+).

A CH\(_3\)NH\(_3\)PbI\(_3\) perovskite layer was deposited on a various different film or substrate, as discussed above, inside a glove box, following the reported method. [Liu 2016 and Wakamiya 2014] A PbI\(_2\) solution with various concentration (1.0 ~ 1.1 M) 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 into a perovskite layer. To remove excess amount of MAI, the films were quickly rinsed with 2-propanol and dried at 70 °C for 30 min. For some films, a hole-transporting layer was deposited on top of TiO\(_2\)-MAPbI\(_3\) by spin-coating a solution of OMeTAD in dehydrated chlorobenzene (0.058 M) without and with 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] \((5.6 \times 10^{-3} M)\). The film was fixed 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.

**Characterization.** Absorption spectra of perovskite deposited films or devices were measured by a UV-Vis absorption spectrometer (Shimadzu, UV-2450). Photoluminescence spectra of the film were collected using a PTI UV-Vis fluorometer (Photon Technology International, Inc.) with slit widths 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.

Nanosecond transient emission spectroscopy (ns-TES) was employed to monitor perovskite excited state decay dynamics. An electron injection or a hole injection from the perovskite
excited state to the TiO$_2$ or the OMeTAD, respectively, was also measured by following the emission quenching dynamics compared to the excited state decays observed for MAPbI$_3$ on a slide glass. Data were obtained by a home-built transient emission spectrometer with a N$_2$ laser (LTB Lasertechnik Berlin GmbH, MNL 202-C) pumped dye laser (LTB Lasertechnik Berlin GmbH, ATM200, 700 ps pulse duration) as an excitation source. The excitation laser pulse was irradiated from the glass substrate side. Emission from a perovskite layer was collected through a monochromator (Acton, Princeton Instruments), and detected by a nanosecond detection system (Unisoku Co., Ltd., TSP-2000SN, time resolution: 1.2 ns (FWHM)) with a fast oscilloscope (Tektronix, TDS 3052C, Digital Phosphor Oscilloscope 500 MHz 5 GS/s) at 10 Hz excitation repetition rate. The emission decay profile was synchronized with the excitation pulse and the detection system using a laser trigger detector. The applied bias dependent transient emission decays for MAPbI$_3$-based perovskite device were performed by using a potentiostat (Ivium Technologies B.V., Compact Stat). FTO glass and gold were employed as a working and counter/reference electrode, respectively. The bias was applied from 0 V with -0.1 V steps following the measurement of the reference line after 15 mins stabilization at 0 V vs. gold.

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 an N$_2$ 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, probe wavelength range: 400-1,100 nm, time resolution: ~700 ns), and a TDS-2022 Tektronix oscilloscope. 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 an 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, probe wavelength range: 900-2,500 nm, time resolution: ~150 ns), and a TDS-3012B Tektronix oscilloscope. 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.
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Excitation wavelength dependent transient emission decays for perovskite excited state. Comparison of effective lifetimes obtained for glass/MAPbI$_3$ excited at various wavelengths by the dependence of excitation intensity.

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Notes

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REFERENCES


Supporting Information

Potential Level Dependent Interfacial Charge-Carrier Dynamics in a CH$_3$NH$_3$PbI$_3$-based Perovskite Film

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Figure S6.1. (a) Excitation wavelength dependent transient emission decays monitored at 770 nm for glass/MAPbI$_3$ film, obtained with excitation intensity of 0.1 $\mu$J cm$^{-2}$. The solid line shows results of fitting with Equation 3 and Equation 4. (b) Comparison of effective lifetimes obtained for glass/MAPbI$_3$ excited at various wavelengths by the dependence of excitation intensity.
Chapter 7 Light Intensity Dependence of Performance of Lead Halide Perovskite Solar Cells

Introduction

In recent years, organic-inorganic halide perovskite solar cells (OHPSCs) have attracted extensive attentions from researchers in both lab scale and industrial area, owing to their high-efficiency performance and ease of low-cost solution processing. Since the power conversion efficiency of OHPSCs have been already improved to be able to compete with conventional silicon solar cells, there are more demands for the commercial application of those high-performance perovskite solar cells. A wide range of applications can be considered for OHPSCs; they are not only applied for outdoor solar power generation system, but also for indoor low power driven devices such as mobile devices or sensors. For the latter case, the operated light level can be different and the corresponding studies under various incident light levels are required. The light intensity as a direct factor significantly influences the performance of any type of solar cells. In Chapter 4, I have demonstrated the influence of excitation intensity on electron and hole injection dynamics in a MAPbI$_3$-based film with mesoscopic structure. It has been identified that both injection yields reduces with the increase of light intensity, resulting in one conclusion that a mesoporous TiO$_2$/MAPbI$_3$ perovskite/spiro-OMeTAD configured solar cells are not suitable for the application of concentrator photovoltaics. However, the literatures hardly show
systematic investigation for the influence of low light intensity on the performance of OHPSCs.

In this chapter, the light intensity dependence (<1.2 sun) of the performance of nanoporous TiO₂ based lead iodide perovskite solar cells has been investigated. The short circuit photocurrent density increases linearly with the light intensity increase, while the fill factor keeps nearly the same over the intensity change. The analysis of the logarithmic light intensity dependence of the open circuit voltage indicates a slope of $1.09kT/q$, which means that the cell operates almost ideally with only bimolecular charge recombination and negligible leakage current. Accordingly, the overall device performance is enhanced by increasing the incident light intensity up to 1.2 sun.

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Performance of nanoporous TiO\textsubscript{2} based lead iodide perovskite solar cells was investigated under a series of light intensity up to 1.2 sun. The short circuit photocurrent increases linearly with the intensity increase, while the fill factor slightly decreases with the intensity increase. The analysis of logarithmic light intensity dependence of the open circuit voltage revealed a slope of 1.09 $kT/q$, indicating ideal function of the present solar cells with only bimolecular charge recombination and negligible leakage current. This analysis further suggests that the solar cell performance is improved by simply increasing incident light intensity up to 1.2 sun.

**Keywords:** Light intensity dependence, CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite solar cells, Internal quantum efficiency, Open circuit voltage

### 1. Introduction

Organometal trihalide perovskite solar cells have received considerable interest as one of the most promising candidates for low cost and high efficiency solar cells. Among them, lead halide based perovskite films exhibit excellent properties such as a narrow band gap, long excited state lifetime and high charge carrier mobility to achieve high solar energy conversion efficiency, and thus have been investigated over the last several years [1-6]. The power conversion efficiency of the lead halide based solar cells has dramatically been improved [7-13], and now exceeds 22%.

A wide range of applications can be considered for the lead halide based solar cells; they are not only applied for outdoor solar power generation system, but also for indoor low power driven devices such as mobile devices or sensors. Those devices are operated under different light levels, and the required performance can be different. For example, the high efficiency performance is required for outdoor power generation systems, operated under one sun to several hundreds of sun for concentrator PVs. Therefore, the studies under different incident light levels are required.

The influence of light intensity on the reaction at the semiconductor films and their solar cell performance has been extensively investigated for dye sensitized solar cells [14], quantum dot sensitized solar cells [15] and bulk heterojunction organic solar cells [16,17], and suitable models have been proposed. We have recently reported the influence of excitation intensity on electron and hole injection dynamics in a mesoporous TiO\textsubscript{2} supported CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite film with a spiro-OMeTAD layer [18]. We have identified both injection efficiencies lowers with the increase of the light intensity, and thus concluded that a mesoporous TiO\textsubscript{2} / CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite / spiro-OMeTAD based solar cells are not suitable to be applied for concentrator PVs. In contrast, there are hardly any reports to systematically investigate the influence of low light intensity on the performance of lead halide perovskite solar cells [19].

In this paper, we demonstrate influence of low incident light intensity on solar cell parameters such as short circuit photocurrent, open circuit voltage and fill factor of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite solar cells. The cell structure employed for this study is shown in Scheme 1. As reported previously [18], a
mesoporous TiO₂ film acts as an electron acceptor following light absorption by the perovskite layer, and also extends charge separation lifetimes.

Scheme 1. Schematic diagram of a CH₃NH₃PbI₃ / mesoporous TiO₂ based perovskite solar cell under illumination with various light intensity.

2. Experimental

2.1. Materials

Anhydrous lead iodide (PbI₂) and CH₃NH₃I (MAI) powder were purchased from Tokyo Chemical Industry, CO., LTD. (TCI). N,N-dimethylformamide, 2-propanol and chlorobenzene were purchased from Wako Pure Chemical Industries Ltd., Japan, 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(acetylacetonate) was purchased from Sigma-Aldrich. A nanocrystalline TiO₂ paste with anatase structure (PST-18NR, particle diameter: ca. 20 nm) for a spin coating was purchased from JGC C&C. Al₂O₃ powder (Aeroxide Alu C, particle diameter: approximately 13 nm) was provided by Evonik Degussa GmbH.

2.2. Device fabrication

Perovskite solar cells were fabricated with a two-step method, following the previous reports [20,21]. A 25 mm × 25 mm FTO (fluorine doped tin oxide) glass substrate was etched with Zn powder and 2 M HCl aqueous solution. A compact TiO₂ layer (c-TiO₂) was deposited on the as-prepared patterned substrate by spray pyrolysis of 0.05 M titanium diisopropoxide bis(acetylacetonate) solution in ethanol at 450 °C [22]. A 200 nm-thick TiO₂ mesoporous film (mp-TiO₂) was formed on the compact layer by spin-coating an ethanol suspension of TiO₂ paste (TiO₂ paste:ethanol = 1.3:5 wt. ratio). The sintered substrate was then transferred into an Ar-filled glovebox for the deposition of CH₃NH₂PbI₃ (MAPbI₃) perovskite layer on the mesoporous TiO₂. Similar to the reported method, the high concentrated solution of PbI₂ (1.1 M) in anhydrous DMF was spin-coated on the surface of the TiO₂ film at 70 °C. After baking at 70 °C for 1 h, the substrate was dipped in a 0.06 M solution MAI in anhydrous propanol for 40 s, converting into a perovskite layer. To remove excess amount of MAI, the substrate was swiftly washed with 2-propanol and baked at 70 °C for 30 min. A hole transfer layer was formed on top of a perovskite layer by spin-coating a solution of spiro-OMeTAD in chlorobenzene (0.059 M) containing 4-tert-butylpyridine (TBP, 0.195 M), lithium bis(trifluoromethylsulphonylimide) (Li-TFSI, 0.0317 M) and tris[2-(1H-pyrazol-1-yl)-4-tert butylpyridine]cobalt(III) (tris[trifluoromethyl-sulfonylimide] (Co(III) complex, 5.8 × 10⁻⁷ M). A gold layer (80 nm) was deposited thermally as a back electrode. Performance of a perovskite solar cell was measured using a 2 mm square mask in air without sealing. Three solar cells were fabricated based on this method, and measurements for each cell were performed on different dates and conducted repeatedly to confirm reproducibility. The device was stored in vacuum, and approximately 7% performance decrease was observed after the device was stored in vacuum for a month.

2.3. Characterization

Absorption spectra of a perovskite solar cell were measured by a UV-Vis absorption spectrometer (Shimadzu, UV-2450). Current density – voltage (J – V) curves were measured under AM1.5G solar simulated light (one sun condition, 100 mW/cm² at 22 ± 2 °C) from a solar simulator (HAL-320, Asahi Spectra Co. Ltd.) and using a source meter (Keithley Instruments Inc.: 2400) [23]. The simulated light power density was calibrated by a reference Si photodiode. Light intensity dependence data were collected by varying light intensity from 0.15 to 1.2 sun by adjusting the power with stainless screen mesh sheets.

3. Results and discussion

3.1. Characterization of a perovskite solar cell
Figure 1 shows the steady-state absorption spectrum of a typical perovskite solar cell (FTO/c-TiO$_2$/mp-TiO$_2$/MAPbI$_3$/OMeTAD/Au). From the previous study [21,24], the film thickness is estimated to be 300 nm. The spectral shape with a shoulder around 750 nm is in agreement with the previous report [18].

![UV-vis absorption spectrum of perovskite (MAPbI$_3$) solar cell. The spectrum was observed where the film is not covered by a gold electrode.](image)

To investigate the influence of light intensity, i.e. the number of generated electrons and holes, on the solar cell performance, current density as a function of applied voltage (J – V) curves of the perovskite solar cell were observed under a variety of incident light intensity (AM1.5G), and are shown in Fig. 2. The light intensity was adjusted from 0.15 to 1.2 sun including 1 sun (100 mW/cm$^2$). The averaged performance data are summarized in Table 1.

![J – V curves observed in dark.](image)

**Table 1. Light intensity dependent performance of a perovskite solar cell (The data are from the reverse scan.).**

<table>
<thead>
<tr>
<th>Light intensity / mW cm$^{-2}$</th>
<th>$J_{sc}$ / mA cm$^{-2}$</th>
<th>$V_{oc}$ / V</th>
<th>FF</th>
<th>PCE / %</th>
<th>$R_s$ / Ω cm$^2$</th>
<th>$R_{sh}$ / kΩ cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>20.8</td>
<td>0.932</td>
<td>0.750</td>
<td>12.07</td>
<td>7.56</td>
<td>3.02</td>
</tr>
<tr>
<td>100</td>
<td>18.8</td>
<td>0.925</td>
<td>0.754</td>
<td>13.11</td>
<td>6.84</td>
<td>3.89</td>
</tr>
<tr>
<td>60</td>
<td>9.93</td>
<td>0.920</td>
<td>0.765</td>
<td>11.65</td>
<td>8.92</td>
<td>7.79</td>
</tr>
<tr>
<td>40</td>
<td>5.97</td>
<td>0.902</td>
<td>0.773</td>
<td>10.39</td>
<td>11.1</td>
<td>12.6</td>
</tr>
<tr>
<td>15</td>
<td>2.37</td>
<td>0.872</td>
<td>0.775</td>
<td>10.62</td>
<td>29.6</td>
<td>21.9</td>
</tr>
</tbody>
</table>

Figure 2a shows the results under the light irradiation. In all cases, the shunt resistance is sufficiently large, so that the leakage of electrons or holes is negligible. Clearly increase of both short circuit photocurrent ($J_{sc}$) and open circuit photovoltage ($V_{oc}$) are observed, as the irradiation intensity increases. Figure 2b shows J – V curves observed in dark. The measurement was conducted immediately after the measurement under each light intensity. We expected identical J – V curves, i.e. no difference in the curves measured in dark. However, the onset voltage appears to increase, as the light intensity for the J – V curves under the simulated light decreases. This observation indicates that the transient charge recombination path must be created owing to the light-induced charge carrier generation. This in turn indicates that the charge recombination reaction is accelerated under the stronger light intensity. Thus, FF decreases under the stronger light intensity.

To assess the influence of the light intensity on the solar cell performance, $J_{sc}$, $V_{oc}$, fill factor (FF)
and power conversion efficiency (PCE) were plotted as a function of light intensity, as shown in Fig. 3. As shown in Fig. 3a, almost linear increase of \( J_{\text{SC}} \) with the light intensity was observed. Note that \( J_{\text{SC}} \) was almost invariant under the forward and reverse voltage scan. As a reference, the maximum \( J_{\text{SC}} (J_{\text{max}}) \) was calculated [25] using the absorption spectrum shown in Fig. 1 with the solar spectrum for each incident light intensity, assuming that the charge separation and collection efficiency of unity, and is shown in Fig. 3a. By comparing this estimated \( J_{\text{max}} \) and the observed \( J_{\text{SC}} \), the average internal quantum efficiency (IQE), i.e. multiplication of the charge separation and collection efficiencies, is calculated using the following equation [26].

\[
J_{\text{SC}} = J_{\text{max}} \times \text{IQE}
\]  

(1)

The results ranging 65~80% are shown in Fig. 3a. The IQE appears to increase with light intensity increase (up to 1.2 sun). We speculate that the loss (20~35%) may originate from insufficient charge separation reaction or charge carrier transport. We have recently reported the influence of excitation light intensity on electron and hole injection efficiencies in a mp-TiO2/MAPbI3/OMeTAD film [18], and have clarified that the high efficiency of the solar cell is essentially achieved by the faster hole injection dynamics. Following this study, although the hole injection efficiency is excitation intensity dependent, we have confirmed the charge

Fig. 3. Influence of incident light intensity on the device performance parameters. (a) Short-circuit current density \( (J_{\text{sc}}) \), maximum \( J_{\text{SC}} (J_{\text{max}}) \) from the absorption spectrum and AM1.5G spectrum (dark green square) and average IQE (red circle: observed by the forward scan, blue triangle: observed by the reverse scan), (b) \( V_{\text{oc}} \), (c) FF, and (d) PCE. The dotted and dashed lines are shown as a guide.
separation efficiency of >98% with the incident light intensity of up to 2 sun. Therefore, we conclude that the insufficient charge carrier transport in the film reduces the IQE.

Figure 3b clearly shows the influence of light intensity on \( V_{OC} \). The reverse scan slightly increases \( V_{OC} \), compared to the forward scan, in agreement with the previous reports [27-29]. \( V_{OC} \) increases as the light intensity increases owing to the increase of generated electrons, thereby increasing the quasi-Fermi level in the TiO\(_2\) [30]. The relationship of \( V_{OC} \) with the light intensity is discussed later. As shown in Fig. 3c, FF decreases with the increase of the light intensity. As discussed earlier, the charge recombination is accelerated with the increase of the light intensity, resulting in the decrease of FF. The reverse scan increases FF, compared to the forward scan. This is consistent with the previous observation reported for any type of MAPbI\(_3\)-based solar cells [28,31,32].

The PCE appears to increase with the increase of the light intensity, as shown in Fig. 3d, suggesting that the increase of IQE and \( V_{OC} \) dominates the overall solar cell performance.

3.2. Influence of light intensity on \( V_{OC} \)

Previously, the light intensity dependence of the \( V_{OC} \) was observed to understand the nature of the charge recombination process, i.e. to distinguish bimolecular and trap assisted charge recombination in polymer bulk-heterojunction solar cells [16,33] and dye sensitized solar cells [14]. Instead of the conventional \( p-n \) junction based model, as reported previously by Koster et al, we employ the expression of \( V_{OC} \) of the solar cell functioning with only bimolecular recombination and negligible leakage current, which can be expressed as the following equation [16].

\[
V_{OC} = \frac{E_{gap}}{q} + \frac{kT}{q} \ln\left(\frac{P_G}{(1-P)\gamma N_C^2}\right) \tag{2}
\]

where \( q \) is the elementary charge, \( k \) is Boltzmann’s constant, \( T \) is temperature, \( N_C \) is the effective density of states, \( P \) is the separation probability of a bound electron-hole pair into free charge carriers, \( G \) is the charge carrier generation rate, \( \gamma \) is Langevin recombination constant, \( E_{gap} \) is the band gap of the semiconductor; in this case, the energy difference between the HOMO of OMeTAD and the TiO\(_2\) conduction band edge. \( P \) and \( \gamma \) are independent of the light intensity, and \( G \) is dependent on the light intensity. Figure 4 shows \( V_{OC} \) as a function of logarithm of the light intensity. The data were fitted using equation (2). The fitted results indicate that \( V_{OC} \) increases with increase of the generated charge carriers, i.e. increase of the electron and hole concentration in the respective semiconductor, while the charge recombination rate may not be significantly increased at <1.2 sun condition [14]. The results also indicate a slope of 1.09 \( kT/q \), suggesting that the performance of the present solar cells is dominated by bimolecular charge recombination, and confirming that this behavior cannot be explained by the \( p-n \) junction based model. This conclusion in turn implies not many trap states available in the film or trap states do not limit the performance. Note that the relatively low shunt resistance (about 3 k\( \Omega \)cm\(^2\)) does not seem to influence the performance under the low light intensity, unlike observed for polymer bulk heterojunction solar cells [33]. This observation therefore suggests that the solar cell performance is improved by increasing the incident light intensity up to 1.2 sun.

![Graph of open-circuit voltage \( V_{OC} \) as a function of incident light intensity](image)

**Light intensity / mW-cm\(^{-2}\)**

In summary, we have investigated light intensity dependence (<1.2 sun) of the performance of nanoporous TiO\(_2\) based lead iodide perovskite solar cells. The short circuit photocurrent density increases linearly with the light intensity increase, while the fill factor slightly decreases with the intensity increase. Analysis of the logarithmic light intensity dependence of the open circuit voltage indicates a slope of 1.09 \( kT/q \), revealing that the cell functions almost ideally with only bimolecular...
charge recombination and negligible leakage current. Based on this analysis, the solar cell performance is improved by increasing the incident light intensity up to 1.2 sun.

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References
Chapter 8 Conclusions and Recommendations

8.1 Conclusions

For this thesis the relationship between interfacial charge transfer dynamics, relevant physical mechanisms and solar cell performance was investigated in the material system MAPbI$_3$-based perovskite film. First of all, excitation intensity dependent charge separation kinetics at the perovskite interfaces have been discussed. Meanwhile, key parameters, i.e. thicknesses of perovskite and mesoporous TiO$_2$ layers, controlling interfacial charge carrier transfer dynamics have been demonstrated in this thesis. Another important aspect is the influence of the potential levels of perovskite and charge selective layers on the charge separation and recombination processes, which is also investigated in the third part of this thesis. Eventually, light intensity dependent performance of MAPbI$_3$-based perovskite solar cells has been illustrated by correlating with the previous study of interfacial charge transfer mechanism. Key contributions of this thesis are summarized as following:

Excitation intensity influencing excited state lifetime and charge injection yield in a MAPbI$_3$-based film: An accelerated excited state lifetime (180 ~ 5 ns) with increased excitation intensity (0.01 ~ 50 $\mu$J cm$^{-2}$) lowers electron (95% ~ 10%) and hole (99% ~ 50%) injections in mp-TiO$_2$/MAPbI$_3$/OMeTAD. Nevertheless, both electron and hole injections occur with nearly 100% efficiency under the AM1.5G on sun condition (100 mW cm$^{-2}$), well explaining the high-performance of perovskite devices. The electron and hole injection rates have been respectively estimated as ~ 11 ns and ~ 1.8 ns that are significantly slower than
those reported using femtosecond transient absorption and terahertz spectroscopies. This difference may originate from multi-phasic electron injection processes \textit{i.e.} more than 3 components over fs–ns time scales, requiring different time scales for observation. Eventually, the charge separated state lifetime was extended with the presence of a TiO$_2$ electron acceptor and an OMeTAD hole acceptors, indicating that their presence really assist maximizing solar cell performance.

**Thickness controlling charge injection rate and charge separated state lifetime at the perovskite interfaces:** The electron injection rate is deaccelerated with the increase of perovskite layer thickness, meanwhile the hole injection rate almost remains constantly swift, mainly contributing to the overall high charge separation efficiency. The charge separated state lifetime is prolonged by increasing the perovskite layer thickness, owing to the complete coverage of perovskite crystals with pin-hole free morphology. The mesoporous TiO$_2$ layer is required to be presented to enhance the electron injection yield while preferring the thinner thickness to accelerate the electron injection rate. The perovskite device performance is essentially controlled by the charge recombination process, \textit{i.e.} longer charge separated state lifetime potentially improves solar cell performance.

**Potential level influencing the charge separation and recombination processes at the perovskite interfaces:** The increase of excitation photon energy accelerates the electron injection rate while the rapid hole injection rate is almost non-sensitive with the excitation energy, owing to the dual valence band model for the hot carriers in excited state perovskite. The CB level of ETM such as TiO$_2$ closing to the CB of perovskite facilitates the efficient electron injection due to the cascade energy structure. With more p-type doping in HTM, the
HOMO level of OMeTAD shifts towards more negative energy level, retarding the charge recombination between an electron in the TiO$_2$ CB and a hole at OMeTAD, supporting maximizing the perovskite cell performance.

**Light intensity influencing the key factors of perovskite device performance:** The short circuit photocurrent density ($J_{sc}$) increases linearly with the light intensity increase (<1.2 sun), while the fill factor remains nearly the same over the intensity range. The logarithmic light intensity dependence of the open circuit voltage ($V_{oc}$) indicates a slope of $1.09kT/q$, suggesting that the cell functions almost ideally with only bimolecular charge recombination and negligible leakage current. In terms of this study, the solar cell performance is improved by enhancing the incident light intensity up to 1.2 sun.

In summary, the underlying mechanism of MAPbI$_3$-based perovskite cell function has been comprehensively elucidated through this thesis study about interfacial charge transfer dynamics at the perovskite interfaces, influenced by several key parameters. For the current solar cell structure of FTO/c-TiO$_2$/m-TiO$_2$/MAPbI$_3$/OMeTAD/Au, it is concluded that the cell performance is essentially controlled by the charge recombination process, i.e. longer charge separated state lifetime potentially improves solar cell performance. Based on the series of interfacial dynamics studies in this thesis, the best cell structure has been proposed. The optimal performance will potentially be obtained by decreasing the thickness of m-TiO$_2$ layer as thin as possible, although this m-TiO$_2$ layer has to be present (to increase the electron injection yield), and by increasing the thickness of perovskite absorber as thick as possible, provided that the thickness is less than 350 nm. Moreover, more p-type doping of HTM, i.e.
Co(III) complex doped spiro-OMeTAD should be employed to prolong the charge separated state lifetime while remaining high hole injection yield.

8.2 Challenges and Recommendations

Organic-inorganic perovskite solar cells have exhibited high efficiency and are being investigated as a viable commercial option. However, the crucial issues and challenges that limited the commercialization of perovskite-based PV remain. Long-term device stability during operation under stressed conditions (high humidity, elevated temperature, and intense illumination) has yet to be demonstrated. The existence of the $J – V$ hysteresis limits the standardized characterization of device performance. Environmental impacts during the manufacturing, operational, and disposal phases of perovskite solar cells are unclear, leaving concerns about the toxicity and contamination associated with the water-soluble lead compounds. Against above listed challenges and issues, several major recommendations have been supplied based on my research outcomes, providing insights to pursue further performance improvement and commercialization of perovskite solar cells.

**Optimization of cell structure and quality of functional layers**: as discussed in Chapter 5, one of the factors influencing the perovskite cell performance is to retard the charge recombination process. Therefore, it is crucial to kinetically control the interfacial charge transfer for both planar heterojunction and mesoscopic structures as currently both structures are equally efficiently designed in the community. Interfacial molecules can be appropriate candidates to be inserted at the interfaces between perovskite and charge selective layers particularly for planar heterojunction structure, since those interfacial molecules can
effectively suppress the charge recombination reactions while remaining high charge separation efficiency. This concept has been widely employed in the development of organic solar cells and organic/inorganic hybrid solar cells. Dye molecules, short alkyl chain organic ligands, and some conjugated polymers are mainly utilized to be the role of interface molecules. However, the strong attachment of interfacial molecules at the perovskite interfaces are still challenging due to the compatibility issue. Further progress in terms of PCE is predicted through improving the crystal structure quality, grain size distribution of perovskite materials along with uniform surface-coverage and careful control of structural and electronic properties of interfaces within device. Besides, the low exciton binding energy and ambipolar charge transport properties of perovskite films enable them to be the suitable candidate for application in tandem cells by employing other PV-applicable semiconductors such as organic PVs, silicon (c-Si or a-Si), copper indium gallium di-selenide (CIGS) and etc.

Alternative of MAPbI$_3$ perovskite nanocrystals that can be used as light absorber in solar cells: it has been well-known that perovskite nanocrystals possess promising intrinsic properties i.e. high quantum yield of photoluminescence and fewer surface and trap state, compared to bulk crystals of perovskite. Therefore, there is a big potential to improve the cell performance by utilizing high quality of perovskite nanocrystals as active layer. But the as-synthesized perovskite nanocrystals generally possess long alkyl chain capping ligands such as oleic acids, which are supposed to be exchanged by short chain ligands, improving the charge separation efficiency. This issue should be effectively solved prior to obtain high quality of stacked perovskite nanocrystals layer for device application.
Development of air-stable and lead-free perovskite solar cells: it has been proved that the organic-inorganic trihalide perovskites are very moisture sensitive and toxic due to the lead element. For future commercialization, the air-stable and lead-free devices are highly demanded. There have been works that cesium-based and tin-based perovskites are developed and used in solid-state perovskite devices, effectively improving the air stability and reducing the toxicity for perovskite solar cells. However, up to now, the performance of those types of solar cells is still quite low. Therefore, there are still existing challenges for making high-performance of perovskite solar cells with high stability and less toxicity.

In all, solar energy as one of the best renewable energy will definitely play a more and more significant role in human being’s life and industry. The perovskite solar cells are one of most promising solar cells that will eventually solve the energy demand on this planet. In a short term of four years, this type of solar cells has achieved a record efficiency of over 22%. Further study and hard works in this region will trigger more outstanding achievements.
Appendix Fluorene-Thiophene Copolymer Sensitized TiO$_2$ Nanohybrid Films: Interfacial Molecular Design Towards Long-Lived Charge Separated State

Introduction

During the last decade, emerging photovoltaics or so called next generation solar cells like dye sensitized solar cells and organic bulk heterojunction solar cells have been widely investigated by means of various engineering methods. Among those methods, one promising approach is termed as “interfacial engineering”. Generally, organic molecules can be the appropriate candidates for the interfacial modification. Insertion of this kind of interfacial molecules in bulk heterojunction and dye sensitized solar cells is effective to retard charge recombination reactions, and thus to improve solar cell performance. The molecular structure is effectively designed to increase distance between an n-type semiconductor and a p-type semiconductor to reduce their electronic coupling.

In the appendix, I propose a novel interfacial molecular structure design by forming a thiophene-fluorene molecular wire on the TiO$_2$ nanoporous surface via a carboxyl group attached to the fluorene unit. The polymer wire acts as a sensitiser aligned in parallel to the TiO$_2$ surface, and injects an electron into the TiO$_2$ with electron injection efficiency of $>80\%$. I found that a generated hole appears to be localized at the thiophene unit which is not
directly attached to the TiO$_2$ surface. Charge recombination between the mobile electron in the TiO$_2$ and the hole at the thiophene unit is retarded to $>100$ ms, compared to the reaction at their monomer/TiO$_2$ interface with $\sim$5 ms. Monte Carlo simulation supports that this slow charge recombination was achieved with the localization of the hole at the thiophene unit requiring to overcome some potential barrier to reach the fluorene unit, assuming that the charge recombination occurs via the fluorene unit. This concept of inserting interfacial donor-acceptor polymer wire can also be applicable to any solution processed planar p-n junction type solar cells such as perovskite solar cells to improve their performance.

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Fluorene—Thiophene Copolymer Wire on TiO₂: Mechanism Achieving Long Charge Separated State Lifetimes

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ABSTRACT: Insertion of interfacial molecules in bulk heterojunction and dye sensitized solar cells is effective to retard charge recombination reactions and thus to improve solar cell performance. So far, to extend charge separated state lifetime, the molecule was designed to increase distance between an n-type and a p-type semiconductors to reduce their electronic coupling. Here we investigated a series of thiophene—fluorene molecular wires on the TiO₂ nanoporous surface and propose a model to explain a long-lived charge separated state. The polymer wire acts as a sensitizer aligned in parallel to the TiO₂ surface and injects an electron into the TiO₂ with electron injection efficiency of >80%. Time-resolved microwave conductivity measurements suggest that a generated hole can be mobile, and we found with DFT calculation that a hole appears to be localized at the thiophene units which are not directly attached to the TiO₂ surface. Charge recombination between the mobile electron in the TiO₂ and the hole at the thiophene units is retarded to >100 ms compared to the reaction at the monomer/TiO₂ interface with ~5 ms. Monte Carlo simulation supports that this slow charge recombination occurs with the localization of the hole at the thiophene units.

INTRODUCTION

Excitonic solar cells such as dye sensitized solar cells and bulk heterojunction polymer solar cells have intensively been developed over the past few decades.¹⁻² Owing to short lifetime and short diffusion length of their excitons generated following light absorption, their structure typically has large interfacial area at which the excitons can readily reach and can be dissociated to generate free charge carriers, fundamentally different from planar conventional solar cells such as crystalline Si solar cells. The free charge carriers must reach their respective electrode or electron/hole transporting layer (blocking layer) without recombining with their countercharges to function as a solar cell. Despite the advantage, such large interfacial area may also act as charge recombination sites before the free carrier reaches an electrode or blocking layer. In a polymer bulk heterojunction solar cell or dye sensitized solar cell, the charge recombination process at the interface is relatively slow, indicating that non-geminate charge recombination dominates the energy loss mechanisms.¹⁻³ Such a recombination mechanism has been explained by the multiple trapping model.⁴⁻⁶

To further improve the cell performance, it is crucial to design the interface for reducing their charge recombination rates, i.e., suppressing probability of charge recombination reactions of free/trapped carriers, following the photoinduced charge separation at the interface. Insertion of interfacial molecules at the interface is one of the most common approaches to reduce the charge recombination rates. Such interfacial structure is shown in Scheme 1a. The interfacial molecule requires relatively narrow HOMO—LUMO gap to absorb visible light; however, their HOMO level should be deeper than the valence band edge of the adjacent p-type semiconductor, and their LUMO level should be shallower than the conduction band edge of the adjacent n-type semiconductor for efficient charge separation. In such a case, the cascade charge transfer occurs upon the excitation of the interfacial molecule. With this interfacial molecule, the distance between the separated electron and hole can be increased to retard charge recombination.

Supporting Information
In this paper, we extend this study and establish a model to explain extremely long charge separated state lifetime by modifying the native molecular structure to retard charge recombination and p-type semiconductors, is sufficiently decreased, thereby \( n \) \( \pi \) \( D \) \( A \) the number of thiophene units is altered to investigate their influence on charge separation and recombination dynamics. In all molecules, a carboxyl group connected to the thiophene unit attaches the TiO\(_2\) surface. The molecular wires were formed by electrochemically polymerizing the attached monomers, similar to the method reported previously.\(^\text{12}\) A donor \((D)\)–acceptor \((A)\) or donor \((D)\)--\(\pi\)--acceptor \((A)\) structure, shown in Scheme 1b, has typically been designed and demonstrated to improve efficiency.\(^\text{8,12} \)\(^\text{18}\) The acceptor unit can efficiently inject an electron to the TiO\(_2\) conduction band, while the donor unit is located further from the TiO\(_2\) surface and can inject a hole to an electrolyte. Transient absorption studies were conducted to explain the influence of the molecular structure on the charge recombination dynamics.\(^\text{3,5,17,18}\) The increase of the distance between the donor unit and the TiO\(_2\) surface extended the charge separation lifetime to \( >1 \) s.\(^\text{15}\) These previous studies suggest that the donor unit and the TiO\(_2\) surface extended the charge separation and recombination dynamics.\(^\text{15}\)\(^\text{16}\)

Previously, as a preliminary study, we reported a fluorescent polymer \((D)\)--\(\pi\)--acceptor \((A)\) or donor \((D)\)--\(\pi\)--acceptor \((A)\) structure, shown in Scheme 1b, has typically been designed and demonstrated to improve efficiency.\(^\text{8,12} \)\(^\text{18}\) The acceptor unit can efficiently inject an electron to the TiO\(_2\) conduction band, while the donor unit is located further from the TiO\(_2\) surface and can inject a hole to an electrolyte. Transient absorption studies were conducted to explain the influence of the molecular structure on the charge recombination dynamics.\(^\text{3,5,17,18}\) The increase of the distance between the donor unit and the TiO\(_2\) surface extended the charge separation lifetime to \( >1 \) s.\(^\text{15}\) These previous studies suggest that the donor unit and the TiO\(_2\) surface extended the charge separation and recombination dynamics.\(^\text{15}\)\(^\text{16}\)

and hole increases, i.e., the electronic coupling between n-type and p-type semiconductors, is sufficiently decreased, thereby delaying the charge recombination process.\(^\text{69}\) Recently, this insertion concept has been demonstrated for polymer bulk heterojunction solar cells,\(^\text{7} \)\(^\text{10}\) i.e., so-called organic ternary solar cells, and hybrid solar cells.\(^\text{70}\) Semiconductor quantum dots were also employed as an insertion particle in polymer bulk heterojunction solar cells.\(^\text{8,12} \)\(^\text{14}\) Generally, the larger \((bulky)\) interfacial molecule or quantum dot is inserted; the slower charge recombination is realized.\(^\text{11}\) In a dye sensitized solar cell, the sensitizer dye not only acts as a light absorber but also functions as an interfacial molecule. The dye molecular structure influences charge separation efficiency, and thus design of the molecular structure is crucial to control the device performance.\(^\text{15} \)\(^\text{18}\) The designed structure is shown in Scheme 1c. A polymer containing donor \((thiophene)\) and acceptor \((fluorene)\) units alternately is located in parallel along the TiO\(_2\) surface, and only fluorene units are connected to the TiO\(_2\) surface. Following the light absorption by this polymer, an electron is efficiently injected from the acceptor unit to the TiO\(_2\), and we found extremely slow charge recombination \((>100 \) ms\).

In this paper, we extend this study and establish a model to explain extremely long charge separated state lifetime by modifying a molecular structure, i.e., by synthesizing a series of fluorene--thiophene copolymer on TiO\(_2\) surface, and by characterizing them with a series of spectroscopies and simulation. In this study, the number of thiophene units is altered to investigate their influence on charge separation and recombination dynamics. In all molecules, a carboxyl group connected to the fluorene unit attaches the TiO\(_2\) surface. The molecular wires were formed by electrochemically polymerizing the attached monomers, similar to the method reported previously.\(^\text{12}\) In this study, the number of thiophene units is altered to investigate their influence on charge separation and recombination dynamics. In all molecules, a carboxyl group connected to the fluorene unit attaches the TiO\(_2\) surface. The molecular wires were formed by electrochemically polymerizing the attached monomers, similar to the method reported previously.\(^\text{12}\) In this study, the number of thiophene units is altered to investigate their influence on charge separation and recombination dynamics. In all molecules, a carboxyl group connected to the fluorene unit attaches the TiO\(_2\) surface. The molecular wires were formed by electrochemically polymerizing the attached monomers, similar to the method reported previously.\(^\text{12}\) In this study, the number of thiophene units is altered to investigate their influence on charge separation and recombination dynamics. In all molecules, a carboxyl group connected to the fluorene unit attaches the TiO\(_2\) surface. The molecular wires were formed by electrochemically polymerizing the attached monomers, similar to the method reported previously.\(^\text{12}\) In this study, the number of thiophene units is altered to investigate their influence on charge separation and recombination dynamics. In all molecules, a carboxyl group connected to the fluorene unit attaches the TiO\(_2\) surface. The molecular wires were formed by electrochemically polymerizing the attached monomers, similar to the method reported previously.
oven at 500 °C for 1 h. The film was then immersed in F(T2)2 ethanol solution (50 μM) or F(T3)2 or F(T4)2 DMF solution (50 μM) for 12 h at room temperature. The film was then thoroughly washed in pure solvent to remove unattached monomers. The film thickness is about 5 μm, measured by a Dektak 6M surface profiler.

**Polymer/TiO2 Hybrid Film Preparation.** Polymer, i.e., molecular wire, and sensitized TiO2 hybrid films were obtained by electrochemical polymerization of the monomers attached to TiO2. A three-electrode cell was fabricated with a Pt counter electrode, Ag/AgCl reference electrode, and a monomer sensitized TiO2 working electrode. Acetonitrile containing 0.1 M lithium perchlorate was poured into the cell as an electrolyte. No further monomer source was added into the system, ensuring that polymerization reaction occurs only between the monomers attached to the TiO2. A positive bias (+1.0 V vs Ag/AgCl) was applied to the film for 10 min, followed by negative bias application (−0.5 V vs Ag/AgCl) for 10 min, using an ALS660 electrochemical analyzer.

**Optical Measurements.** Steady-state absorption spectra were measured by using a JASCO V-670 spectrometer. Steady-state emission spectra were measured with a Horiba SPEX Fluorolog-3.

**Density Functional Theory (DFT) Calculation.** DFT calculation was conducted with Gaussian 09 program package, using the supercomputer “Raijin” in National Computational Infrastructure (NCI), Australia. Geometry optimization was performed using the Becke’s three-parameter hybrid functional with the Lee—Yang—Parr gradient-corrected functional (B3LYP) and 6-31G(d) basis set. On any monomer structure, symmetry constraints were not imposed. The molecular structure optimizations were followed by the energy calculations. The output molecular orbitals were visualized with a Winmostar.

**Transient Absorption Measurement.** To probe charge separated states and charge recombination kinetics, submicro- to millisecond transient absorption spectroscopy (smm-TAS) measurements were conducted. Time-resolved photoinduced absorption was obtained from a home-built transient absorption spectrometer, as reported in previous studies.

A Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-11) pumped dye laser (Usho Optical Systems, DL-100, ~10 ns pulse duration, ~30 μJ/cm², 0.5 Hz) was employed as a wavelength tunable excitation source, and excitation wavelengths were determined at the peak position of steady-state absorption spectra for each sample. For probe light, a tungsten lamp (Olympus, 100 W) with two monochromators equipped with band-pass filters was employed. Optical signal change (ΔOD) was detected with a photodiode-based detection system (Costronics Electronics) and an oscilloscope (TDS-2022, Tektronix). The excitation energy adjustment was finally confirmed by obtaining a transient absorption amplitude of ~1.0 mΔOD at 800 nm using the TiO2 film sensitized by cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II), N3 (Solaronix), for each excitation wavelength, following the previous reports. No change in steady-state absorption spectra before and after the transient experiments was observed, suggesting that the samples were stable during the optical experiments.

**Time-Resolved Microwave Conductivity (TRMC) Measurements.** The charge conductivity (for both holes and electrons) in a monomer or polymer sensitized TiO2 composite was measured by the TRMC system. A sample was placed at the highest electric field in a microwave resonant cavity (resonant frequency 9.1 GHz) and was excited by a third-harmonic Nd:YAG laser pulse (355 nm, Spectra-Physics Inc., INDY, 5–8 ns pulse duration, excitation frequency 10 Hz). The change of the conductivity was obtained by measuring the change of reflected microwave power, ΔPr, with a microwave power of 3 mW as a function of time after the excitation. The obtained ΔPr was converted to ϕ∑μ, where ϕ is the yield of 221 charge separation, i.e., a hole in the monomer or polymer and 222 an electron inside the TiO2, and ∑μ is the sum of hole and 223 electron mobilities. Monomer or polymer sensitized TiO2 film was 224 on a FTO substrate was prepared with the method described 225 in the above section. The sensitized TiO2 film was stripped off 226 from the FTO substrate. Finally, a sample was prepared by 228 drop-casting a poly(methyl methacrylate)—toluene solution 229 containing a monomer or polymer sensitized TiO2 on a quartz 230 substrate. All samples were measured under an ambient con- 231 dition at room temperature.

## RESULTS

**Characterization of Monomer (F(T2)2, F(T3)2, F(T4)2) and Polymer (PFT4, PFT6, PFT8).** Chemical structures of the synthesized fluorene—thiophene monomers and the polymers, i.e., molecular wires, are shown in Scheme 2. For the monomers

Scheme 2. Molecular Structure of Monomers (F(T2)2, F(T3)2, F(T4)2) (m = 1; n = 2, 3, 4) and Polymers (PFT4, PFT6, PFT8) (1 ≪ m; n = 2, 3, 4)

(m = 1), the thiophene unit number, n, is altered from n = 2 to 4. The monomer is named as F(T2)2, F(T3)2, or F(T4)2 based on the thiophene unit number beside the fluorene unit. Upon sensitization, the fluorene unit attaches the TiO2 surface through the carboxyl group, and the thiophene—fluorene—thiophene molecule lies along the TiO2 surface. To form a polymer, a positive bias was applied to the attached F(T2)2, F(T3)2, or F(T4)2 (see the Supporting Information for the details). The neighboring monomers were oxidized and connected (oxidation polymerization), forming polymer (pFT4, pFT6, pFT8), where 1 < m. FT4 in pFT4 indicates one fluorene and four thiophene units in one segment of the polymer backbone. Note that we are unable to control the polymerization degree.

The monomers in solution were characterized by steady-state absorption and emission spectroscopy (see the Supporting Information). Figure S1 shows the results. The HOMO—LUMO gap of the monomer was estimated from the absorption onset and decreases with the increase in the thiophene units. Two prominent peaks with two shoulders at longer wavelength lengths were observed for each monomer in the emission spectra. These peaks have been observed as typical emission bands for the corresponding polymers.

Figure 1 compares normalized absorption spectra of the 261 monomer or polymer sensitized TiO2 films, while the absorption 262
The absorption spectra of the respective Al2O3 films are shown in Figure S2. The F(T2)2, F(T3)2, and F(T4)2 sensitized TiO2 films show the absorption peaks at 392, 426, and 448 nm, respectively, almost identical to that of the monomer in solution (Figure S1) and the respective Al2O3 films. This observation suggests that the monomer does not electronically interact with the TiO2 upon the attachment, and also no interaction is established between the attached monomers.

Under the electrical bias application, the absorption band is significantly broadened with the red-shifted absorption onset of approximately 560, 590, and 600 nm for pFT4, pFT6, or pFT8, respectively, indicative of successful polymerization of the monomers, although the absorption peaks (392, 441, and 440 nm) are similar to the monomer. The spectral absorption broadening is the smallest for the pFT8, suggesting that the influence of the conjugation from T4 to T8 is relatively small. This observation is plausible, since the transition energy of thiophene oligomers decreases linearly with the inverse thiophene ring numbers. With this electrochemical polymerization method, we can maintain the sensitized structure between the monomer and the molecular wire, e.g., the distance and orientation between the chromophore and the TiO2 surface are almost identical, and thus interfacial charge transfer and transport dynamics can solely be assessed based on the link between the monomers.

The HOMO–LUMO gap energy of the monomer or polymer attached TiO2 was estimated from the absorption onset of each spectrum and is summarized in Table 1. They are also almost identical to those obtained from the solution phase (Figure S1) and the Al2O3 films (Figure S2). These HOMO–LUMO gap energy has been correlated with the reciprocal of the thiophene unit numbers (Figure S3), suggesting that the HOMO–LUMO gap energy is essentially determined by the thiophene unit length.

We also employed cyclic voltammetry and spectroelectrochemical measurements to determine the first oxidation potential (HOMO) of the monomer and the formed polymer, respectively (Table 1). The results of the cyclic voltammetry and spectroelectrochemical measurements are shown in Figures S4 and S5 of the Supporting Information. With the estimated HOMO–LUMO gap energy and HOMO level, the LUMO level can be estimated and shown in Table 1.

**Electron Injection.** The electron injection reactions are monitored and determined by photoluminescence spectroscopy. Photoluminescence measurements were conducted for a monomer or polymer sensitized TiO2 film in comparison with a monomer or polymer attached nanocrystalline Al2O3 film (as a reference sample) whose absorption spectrum is shown in Figure S2. Upon the polymerization, the absorption peak and onset are red-shifted compared to the monomer spectra. Figure 2 shows emission spectra for the monomer or polymer sensitized TiO2 film and the monomer or polymer attached Al2O3 film. Since Al2O3 is an insulator, no charge transfer process is expected, and thus as expected, the monomer and polymer attached Al2O3 films show strong photoluminescence. On the other hand, the emission amplitude for any TiO2 film is significantly reduced owing to the faster electron injection reaction than the excited state decay. By comparing these spectra, the electron injection efficiency was estimated, assuming that the emission quench solely originates from the electron injection reaction. The results are summarized in Table 2.

DFT calculation was conducted to identify electronic density distribution of the frontier orbitals of the monomer. The optimized molecular structures (symmetric) and frontier orbitals are shown in Figure 3. All the LUMOs show antibonding character between the bridge atoms of the fluorene and thiophene units, and a LUMO orbital is delocalized over the entire molecule, in agreement with the DFT studies conducted for the fluorene–thiophene oligomers. In contrast, the HOMO indicates the different profile, showing antibonding character between the bridge atoms. A HOMO orbital is delocalized over the entire molecule for F(T2)2, while the orbital is gradually localized on the thiophene units with the increase of the unit number for F(T3)2 and F(T4)2. This result implies that the HOMO of F(T3)2 and F(T4)2 is less planar between the fluorene and the thiophene units, compared to F(T2)2.
and may suggest that upon polymerization a HOMO–LUMO orbital is most likely localized on the thiophene units.

Following the electron injection process, the charge separated state of the monomer or polymer sensitized film was observed using submicrosecond–millisecond transient absorption spectroscopy (smm-TAS). Figure 4 shows transient absorption spectra of the monomer or polymer sensitized TiO2 films at 2 μs after the excitation. Since the excited state decays on early nanoseconds (data are not shown), all of the spectra are assigned to the charge separated state, i.e., an electron in the TiO2 and the monomer or polymer cation/polaron. Since the extinction coefficient of an electron in the TiO2 is small (≈3400 M−1 cm−1),21,25,26 the contribution of the absorption by the electrons in the TiO2 is negligible, and therefore the positive amplitude with peak positions at 650, 700, and 750 nm for F(T2)2, F(T3)2, and F(T4)2, respectively, and at 800, 850, and 880 nm for pFT4, pFT6, and pFT8 films, respectively (absorption peak). The number of photons absorbed at the excitation wavelength is corrected for quantitative comparison between the TiO2 and Al2O3 films.

Table 2. Summary of Charge Transfer and Transport Reactions in the Monomer or Polymer Sensitized TiO2 Films: Electron Injection Efficiency, Hole Mobility, Fitted Charge Recombination Lifetime, Stretched Parameter, and Their Simulated Data

<table>
<thead>
<tr>
<th>sample</th>
<th>electron injection efficiency ϕ (%)</th>
<th>$ϕΣμ_{max}$ (μm2 V−1 s−1)</th>
<th>hole mobility $μ_{max}$ (μm2 V−1 s−1)</th>
<th>charge recombination lifetime τ (ms)</th>
<th>stretched parameter α</th>
<th>simulated lifetime τ (ms)</th>
<th>simulated α</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(T2)2</td>
<td>91</td>
<td>1.03</td>
<td>0.13</td>
<td>2.50</td>
<td>0.36</td>
<td>2.5 ± 0.1</td>
<td>0.70</td>
</tr>
<tr>
<td>F(T3)2</td>
<td>90</td>
<td>2.05</td>
<td>1.27</td>
<td>0.86</td>
<td>0.28</td>
<td>1.2 ± 0.1</td>
<td>0.58</td>
</tr>
<tr>
<td>F(T4)2</td>
<td>92</td>
<td>2.41</td>
<td>1.62</td>
<td>4.80</td>
<td>0.24</td>
<td>5.0 ± 0.1</td>
<td>0.78</td>
</tr>
<tr>
<td>pFT4</td>
<td>82</td>
<td>4.09</td>
<td>3.98</td>
<td>123</td>
<td>0.46</td>
<td>123 ± 3</td>
<td>0.98</td>
</tr>
<tr>
<td>pFT6</td>
<td>98</td>
<td>1.72</td>
<td>0.76</td>
<td>163</td>
<td>0.40</td>
<td>163 ± 4</td>
<td>0.93</td>
</tr>
<tr>
<td>pFT8</td>
<td>83</td>
<td>1.07</td>
<td>0.29</td>
<td>171</td>
<td>0.42</td>
<td>170 ± 3</td>
<td>0.92</td>
</tr>
</tbody>
</table>

To assign the transient absorption spectra for the polymer sensitized TiO2 films, differential absorption spectra of oxidized polymers were measured by applying positive electrical bias to the polymer sensitized TiO2 electrode with the spectroelectrochemical method (for experimental details, see the Supporting Information). Note that the spectra of the oxidized monomer states cannot be obtained by this method, since polymers are readily formed once the positive bias is applied to the monomer sensitized electrode. Figure S5 shows absorption difference spectra of polymer (pFT4, pFT6, pFT8) sensitized TiO2 film electrode under the bias application. The negative signal growth can be assigned to gradual loss of the polymer neutral states (ground state bleach), while the positive growth must originate from increased absorption by the polymer oxidized states. Figure S6 compares transient absorption spectra of polymer (pFT4, pFT6, pFT8) sensitized TiO2 film electrode with the spectra of polymer (pFT4, pFT6, pFT8) oxidized states obtained under the bias application of +0.7 V vs Ag/AgCl into the polymer sensitized TiO2 film electrode. The comparison clearly indicates that both transient absorption and oxidized state spectra are almost identical, thereby justifying that the transient spectra shown in Figure 4 indicate charge separated states.

Figure 2. (a–c) Normalized emission spectra of F(T2)2, F(T3)2, F(T4)2, pFT4, pFT6, or pFT8 attached Al2O3 films (dotted line) and the same monomer or polymer sensitized TiO2 films (solid line). The excitation wavelength was 395, 432, and 449 nm for the F(T2)2, F(T3)2, and F(T4)2 films and 392, 441, and 440 nm for the pFT4, pFT6, and pFT8 films, respectively (absorption peak).

Figure 3. Frontier molecular orbitals of F(T2)2, F(T3)2, and F(T4)2 obtained from DFT calculations.
Charge Recombination. Charge recombination dynamics of photoinduced charge separated states at the monomer/TiO₂ or polymer/TiO₂ interfaces were observed by submicro- to millisecond transient absorption spectroscopy (smm-TAS). Transient absorption decays were observed at the peak absorbance of the oxidized monomer or polymer and are compared in Figure 5. The decay kinetics of the monomer sensitized TiO₂ films are similar to that of N₃ sensitized TiO₂ film, although F(T₃)₂ indicates slightly faster charge recombination. In contrast, all of the polymer sensitized TiO₂ films show extremely long lifetimes. These decay dynamics with relatively long lifetimes are clearly different from geminate charge recombination of bound charge pairs observed for polymer bulk-heterojunction films, or Langevin-like pure bimolecular recombination, however probably similar to nongeminate recombination reactions observed for some polymer bulk-heterojunction films. Since these decays indicate typical multiple trapping recombination behavior observed for dye sensitized TiO₂ films, they are therefore fit with a stretched exponential function, \( \Delta OD(t) = \Delta OD_0 e^{-\left(t/\tau\right)\alpha} \) where \( \Delta OD(t) \) is the differential optical density at time \( t \), \( \Delta OD_0 \) is the initial transient absorption amplitude, \( \tau \) is the characteristic stretched lifetime, and \( \alpha \) is stretched parameter. The fitted results are summarized in Table 2.

Charge Carrier Mobility. Upon charge separation, an electron can move inside the TiO₂ nanoparticle, and a hole can be transported along the molecular wire. These charge carrier transports potentially influence charge recombination dynamics and thus the device function. To assess charge carrier mobilities, transient conductivities of photogenerated electrons and holes were measured by the TRMC technique (for experimental details, see the Supporting Information). Figure S7 shows typical photoconductivity decays of (a) the monomer and (b) the polymer sensitized TiO₂ films excited at 355 nm with excitation energy density of 450 μJ/cm², where \( \sum \mu \) is the sum of charge carrier mobility (\( \sum \mu = \mu_+ + \mu_- \)) and \( \phi \) is the charge carrier generation yield including the electron injection yield. With 355 nm excitation, both TiO₂ and monomers/polymer sensitized films show long lifetimes. These decay dynamics with relatively long lifetimes are clearly different from geminate charge recombination of bound charge pairs observed for polymer bulk-heterojunction films or Langevin-like pure bimolecular recombination, however probably similar to nongeminate recombination reactions observed for some polymer bulk-heterojunction films. Since these decays indicate typical multiple trapping recombination behavior observed for dye sensitized TiO₂ films, they are therefore fit with a stretched exponential function, \( \Delta OD(t) = \Delta OD_0 e^{-\left(t/\tau\right)\alpha} \) where \( \Delta OD(t) \) is the differential optical density at time \( t \), \( \Delta OD_0 \) is the initial transient absorption amplitude, \( \tau \) is the characteristic stretched lifetime, and \( \alpha \) is stretched parameter. The fitted results are summarized in Table 2.

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The fitted results are shown in Figure S7. Note although these
decays were also fit with a single exponential or a stretched
exponential function, they did not show comfortable fitting
results (minimum errors). These observations suggest that the
recombination process of free electrons (in the TiO2 con-
duction band) injected from the monomer/polymer and holes
in the monomer/polymer is responsible for these decays; i.e.,
the reaction occurs on a second order. The maximum values
of the injection electron and hole mobility of the
monomer or polymer sensitized TiO2 film. A series of the simulated
values were obtained for each sensitized film by altering excita-
tion energy density, corrected with the number of photons
absorbed by the film, and by extracting the amplitude at t = 0 s
after fitting the decays with a second-order rate equation,
\( \phi \sum \mu_{\text{max}} = \phi \sum \mu_{\text{max}} / (1 + at) \). The resultant values are
plotted in Figure 6. We assume that the electron injection
efficiency is invariant with the excitation intensity. The
results indicate that the transient conductivity slightly decreases
as the excitation intensity increases, implying that the popula-
tion of the free charge carrier decreases owing to fast electron
and hole recombination with the higher excitation intensity.
Katoh et al. conducted TRMC measurements for N719 dye
sensitized nanocrystalline TiO2 (particle size 20 nm) films and
observed the electron mobility (in the TiO2 conduction band)
of approximately 0.01 cm2 V−1 s−1. This mobility value of the
injected electrons can be applicable to all the films we investigat-
ged here, indicating that the difference in the mobility sum
shown in Figure 6 must originate from the difference in hole
mobility of each monomer or polymer. The hole mobility of the
F(T2)2 sensitized TiO2 film is almost negligible, indicating
that a hole is delocalized over the entire molecule and thus is
not mobile. The hole mobility of the monomer increases with
increase of the thiophene unit number. This observation is
plausible since the molecular/conjugation length increases.
The hole mobility reaches the maximum for the pFT4, as the
conjugation length further increases upon the formation of the
polymer wire; however, the mobility decreases for pFT6 and
pFT8. This mobility decrease suggests that a conjugation length
is limited by increasing a thiophene unit number, implying that
a hole is most likely localized over the thiophene units, and a
potential barrier exists for a hole to move from the thiophene to
the fluorene unit. This hypothesis will be supported by charge
recombination dynamics and the simulation study in the
following sections.

Simulation for Charge Recombination Reactions. As discussed in the “Charge Recombination” section, the dynamics of the charge recombination between a hole in the monomer or polymer and an electron in the TiO2 is not similar to geminate recombination of bound charge pairs nor to pure bimolecular recombination. It is rather similar to the dynamics in dye sensitized TiO2 films, i.e., controlled by multiple trapping of an electron in the TiO2. This multiple trapping model has been developed and theoretically applied to explain charge recombination dynamics in dye sensitized TiO2 films using Monte Carlo simulation. Here, we apply Monte Carlo simulation using a random walk model to the monomer or polymer sensitized films to explain the mechanism as to how the charge recombination occurs. The details of the simulation are described in the Supporting Information. In the present model (Scheme S1), to simplify the random walk simulation and to clarify the influence of the hole movement on the recombination rate, we do not consider the distribution of electron trap state energy levels in the TiO2. One pair of electron and hole is available for the simulation.

A simulation completes when a hole arrives at the fluorene unit and an electron arrives at the state beside the hole occupied fluorene simultaneously, i.e., provided that charge recombination occurs via a through-bond electron transfer reaction. All the simulated charge separated lifetimes are plotted in Figure 7, in comparison with the experimental charge recombination decays shown in Figure 5. The simulation results qualitatively reproduced the charge recombination dynamics obtained from the TAS study. The stretched exponential lifetime and stretched parameter for each sensitized film were evaluated from the simulated results and are summarized in Table 2. The simulated lifetime is almost identical to the experimentally obtained lifetime for any film, suggesting that the random walk model for an electron and a hole with the respective waiting time is appropriate to explain the charge recombination rates. In contrast, the stretched parameter obtained from the simulation is 2–3 times larger compared to that obtained from the TAS measurement. For the polymer sensitized films, the simulated charge recombination dynamics indicates almost single exponential (i.e., \( \alpha \approx 1 \)). As described above, since the distribution of electron trap state energy levels in the TiO2, which usually decreases a stretched parameter, is not included in the simulation model, it is reasonable to obtain the increased stretched parameters.

Figure 6. Excitation density dependence of \( \phi \sum \mu_{\text{max}} \) for (a) F(T2)2, F(T3)2, and F(T4)2 and (b) pFT4, pFT6, and pFT8 sensitized TiO2 films with 355 nm excitation.
DISCUSSION

Electron Injection Reaction. Using the monomer and polymer ground-state and excited-state oxidation potentials presented in Table 1, a potential level diagram for the monomer or the polymer sensitized film is shown in Scheme 3, and it is clear that all the LUMO levels are more negative compared to the TiO₂ conduction band edge. From the photoluminescence quenching results shown in Figure 2, all films indicate that the electron injection efficiency exceeds 80%, although no correlation appeared between the LUMO level and the electron injection efficiency. Note that even if an exciton state is initially formed upon photoexcitation, the driving force of the electron injection shown in Table 1 must be sufficient to influence the electron injection efficiency.

From the DFT calculation results to describe the LUMO orbital in Figure 3, an electron is delocalized over the entire molecule including a fluorene unit, justifying that the overlap of wave functions between the LUMO and the conduction band is almost identical among these monomers. We assume that the LUMO of the polymer is similar to those of the monomers. The injection therefore occurs from the LUMO.

Charge Recombination Mechanism. From the TAS results shown in Figure 5, the monomer sensitized films show a lifetime of 1–5 ms with a stretched parameter of 0.25–0.35, while a lifetime of the polymer sensitized film remarkably exceeds 100 ms with a stretched parameter of 0.4–0.5. The lifetime of the polymer sensitized film has extended up to 2 orders of magnitude compared to those of the monomer sensitized films and indicates one of the longest lifetimes observed for the dye sensitized films. The long lifetimes are usually achieved by designing a sensitizer dye with donor (D)–π-acceptor (A) structure aligning vertical to the TiO₂ surface. In the present study, we found that the long lifetime can be achieved for the polymer wire with donor (D)–π-acceptor (A) units aligning parallel to the TiO₂ surface. Also, the increase of the stretched parameter suggests that the magnitude of the TiO₂ electron trap states involved in the charge recombination reactions becomes less, indicating that the charge recombination of the polymer sensitized films is controlled not only by detraping of the electron in the TiO₂ but also by the hole movement movement in the polymer.

Figure 3 suggests that upon polymerization a HOMO orbital is localized on the thiophene units, since the HOMO of F(T3)₂ and F(T4)₂ is less planar between the fluorene and the thiophene units compared to F(T2)₂. The TRMC data shown in Table 2 also suggest that the hole mobility of the F(T2)₂ sensitized TiO₂ film is almost negligible, indicating that a hole is delocalized over the entire molecule and thus is not mobile. In contrast, for other monomers and the polymers, the hole mobility can be observed, indicating that a hole can move between the thiophene and the fluorene units. The hole mobility of the polymer sensitized film decreases, as the thiophene unit number increases. This mobility decrease suggests that a conjugation length is limited at the thiophene units in the polymer, implying that a hole is most likely localized over the thiophene units. These results suggest that the charge recombination occurs between a mobile electron inside the TiO₂ and the hole localized at the thiophene unit except for the F(T2)₂ sensitized TiO₂ films.

The Monte Carlo simulation results for the monomer and polymer sensitized films were used to globally fit the electron waiting time, resulting in 2.3 μs. The fitting of the hole waiting time was also performed for each monomer and polymer sensitized film, and the results are shown in Table S1. For F(T2)₂, the hole waiting time is similar to the electron waiting time, although the hole mobility is significantly smaller than the electron mobility, suggesting that a hole is almost delocalized over the entire molecule. In contrast, the hole waiting time for F(T4)₂ and all the polymer sensitized films is significantly longer than the electron waiting time, suggesting that the activation energy for a hole to move from the thiophene to the fluorene units is significantly large. This in turn suggests that a generated hole is mainly localized at the thiophene units for these films. This result agrees well with the DFT calculation.

![Scheme 3. Potential Level Diagram of Monomers, Polymers, and TiO₂](image)
results for the HOMO orbital shown in Figure 3 and with the TRMC results. We therefore conclude that the hole localization at the thiophene units dominates the charge recombination lifetime for the monomer and polymer wire sensitized systems.

CONCLUSION

A series of interfacial molecular structures, a thiophene–fluorene molecular wires, at a p–n junction were designed to establish a model to explain extremely long charge separated state lifetime. This molecular wire was formed electrochemically from the reaction of the monomers attached to the TiO₂ nanoporous surface and thus aligned parallel to the TiO₂ surface.

A series of spectroscopic studies and DFT calculation results suggest that the charge separation reaction occurs from the polymer LUMO state with electron injection efficiency of >80%. A generated hole can be mobile but most of the time is localized at the thiophene units. By forming a polymer wire, the charge recombination rate is significantly retarded to >100 ms, even if the polymer wire is close to the TiO₂ surface, compared to the monomer sensitized film of ~5 ms. The Monte Carlo simulation suggests that this slow charge recombination was achieved with the localization of the hole at the thiophene units requiring to overcome a potential barrier to reach the fluorene unit, provided that the charge recombination occurs between the mobile electron in the TiO₂ and the hole at the thiophene units.

A polymer wire containing donor–acceptor units can be a rational design as an interfacial molecule inserted in bulk-heterojunction and dye sensitized solar cells, improving the performance by retarding charge recombination reactions while maintaining high charge separation efficiency. This concept is applicable even to any solution processed planar p–n junction type solar cells such as perovskite solar cells, as long as the charge recombination reaction at the p–n junction interface limits their efficiency.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b07295.

Synthesis of monomers, experimental methods describing preparation and polycondensation of monomer attached Al₂O₃ hybrid film, electrochemical measurements and Monte Carlo simulation, and their results (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

Electronic Supporting Information

Fluorene-Thiophene Copolymer Wire on TiO₂: Mechanism Achieving Long Charge Separated State Lifetimes

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1. Synthesis of monomers

F(T2)2 and F(T3)2 were prepared according to our reported procedure,\(^1\) as shown in the above synthetic scheme. F(T4)2 was prepared from 2,7-bis(2-bromobithiophene) fluorene-9,9’-dipropionic acid di-tert-butyl ester\(^1\) via the same Suzuki-Miyaura cross coupling reaction and deprotection.

2,7-bis(bithiophene)fluorene-9,9-dipropionic acid (F(T2)2)

\(^1\)H NMR (400MHz, DMSO-\(d_6\), 28.4 °C): \(\delta_H = 11.84\) (bs, 2H, COOH), 7.90 (d, \(J = 8.2\) Hz, 2H), 7.86 (s, 2H), 7.71 (d, \(J = 8.2\) Hz, 2H), 7.63 (d, \(J = 3.6\) Hz, 2H), 7.54 (d, \(J = 5.1\) Hz, 2H), 7.39 (d, \(J = 3.4\) Hz, 2H), 7.36 (d, \(J = 3.6\) Hz, 2H), 7.13 (dd, \(J = 3.4, 5.1\) Hz, 2H), 2.44 (4H, overlapped with solvent), 1.44 (t, 4H).
2,7-bis(terthiophene) fluorene-9,9-dipropionic acid (F(T3)2)

$^1$H NMR (400MHz, DMSO-$d_6$, 19.8 °C): $\delta_H = 11.90$ (bs, 2H, COOH), 7.91 (d, $J = 8.0$ Hz, 2H), 7.87 (s, 2H), 7.71 (d, $J = 8.0$ Hz, 2H), 7.65 (d, $J = 3.8$ Hz, 2H), 7.55 (d, $J = 5.1$ Hz, 2H), 7.31 (d, $J = 3.8$ Hz, 2H), 7.37-7.35 (m, 4H), 7.31 (d, $J = 3.8$ Hz, 2H), 7.07 (dd, $J = 3.8$ 5.1 Hz, 2H), 2.44(4H, overlapped with solvent), 1.43 (t, 4H)
2,7-bis(tetrathiophene) fluorene-9,9-dipropionic acid (F(T4)2)

$^1$H NMR (400MHz, DMSO-$d_6$, 20.3 °C): $\delta_H = 11.91$ (bs, 2H, COOH), 7.92 (d, $J = 8.0$ Hz, 2H), 7.86 (s, 2H), 7.72 (d, $J = 8.0$ Hz, 2H), 7.68-7.11 (m, 18H), 2.44(m, 4H, overlapped with solvent), 1.44 (m, 4H)
2. Experimental

2.1 Preparation of monomer attached nanocrystalline Al$_2$O$_3$ film

Al$_2$O$_3$ nanocrystalline films, thickness: 7 µm, were prepared using Degussa Aluminum Oxide (Alu C, γ-Al$_2$O$_3$: 67%, δ-Al$_2$O$_3$: 33%, tetragonal crystal system, particle diameter of approximately 13 nm) on a FTO substrate by the screen-printing method following the previously reported methods.$^{1-3}$ The printed Al$_2$O$_3$ films were calcined at 500 °C for 1 h in an air flow oven. Attachment of monomers on the Al$_2$O$_3$ surface was performed by dipping a film in 50 µM F(T2)2 dissolved in ethanol, or F(T3)2 or F(T4)2 dissolved in DMF for 12 hours at room temperature. The film was then thoroughly washed in pure solvent to remove unattached monomers.

2.2 Electrochemical polymerization of monomer attached Al$_2$O$_3$ hybrid films

A three electrode cell was assembled with a Pt counter electrode, a Ag/AgCl reference electrode and monomer adsorbed Al$_2$O$_3$ film working electrode. Acetonitrile containing 0.1 M lithium perchlorate as an electrolyte was added into the cell. A positive bias (+1.0 V vs. Ag/AgCl) was applied to the monomer film for 10 min, followed by negative bias application (-0.5 V vs. Ag/AgCl) (to undope the anion or to neutralize the polymer) for 10 min, using ALS S660 electrochemical analyzer.

2.3 Electrochemical Measurements

Cyclic voltammetry of monomer (F(T2)2, F(T3)2 and F(T4)2) solution was performed in a three-electrode electrochemical cell containing 1 mM monomer and 0.1 M Bu$_4$NPF$_6$ (supporting electrolyte) in a mixture solvent of acetonitrile/ethanol (1:1, vol%) for F(T2)2, or acetonitrile/DMF (1:1, vol%) for F(T3)2 and F(T4)2, using a potentiostat (Ivium Technologies B.V., Compact Stat). A platinum rod (active area: 0.020 cm$^2$), a platinum wire and Ag/AgCl
electrode was employed as a working, counter and reference electrode, respectively. The measurements were conducted in N₂ atmosphere with a scan rate of 50 mVs⁻¹. CV without monomers was also measured as a reference.

Spectroelectrochemical measurements for pFT4, pFT6 and pFT8 were performed in an optical cell with a three-electrode system. The three-electrode system consists of a polymer deposited TiO₂ film on a FTO substrate as a working electrode (prepared by the above method), a platinum wire as a counter electrode and a compact Ag/AgCl as a reference electrode. Acetonitrile containing 0.1 M lithium perchlorate as a supporting electrolyte was filled in the cell. The spectroelectrochemical cell was settled in an absorption spectrometer (JASCO V-670). The polymer deposited TiO₂ film was prepared by the method mentioned in the main text, and used as a working electrode. The bias was applied from 0 V to +1 V with +0.1 V steps following the measurement of the reference line after 15 min stabilization at 0 V vs. Ag/AgCl. The absorption difference spectra were obtained by subtracting this reference line from the spectrum observed at the applied bias after 10 min stabilization. The measurement was conducted under nitrogen flow.
3. RESULTS

3.1 Absorption and emission spectra of the monomer in solution

Figure S1a shows normalized steady-state absorption spectra of F(T2)2, F(T3)2 and F(T4)2. The absorption peaks are 395 nm, 432 nm and 450 nm, respectively. This red shift indicates that the conjugation length of the monomer is extended gradually by increasing the thiophene units, in agreement with the previous reports. Figure 1b demonstrates the normalized emission spectra of F(T2)2, F(T3)2 and F(T4)2. Similar to the absorption spectra, the emission peak wavelength is red-shifted by increasing the thiophene units.

Figure S1. (a) Normalized absorption spectra of F(T2)2, F(T3)2 and F(T4)2 in solution. (b) Normalized emission spectra of F(T2)2, F(T3)2 and F(T4)2 in solution. The excitation wavelength was 395, 432 and 450 nm for F(T2)2, F(T3)2 and F(T4)2, respectively (the absorption peak). F(T2)2 was dissolved in ethanol (10 µM) while F(T3)2 and F(T4)2 were dissolved in DMF (10 µM).
3.2 Absorption spectra of monomer and polymer deposited Al₂O₃ films

Figure S2 shows absorption spectra of monomer (F(T2)₂, F(T3)₂, F(T4)₂) or polymer (pFT4, pFT6, pFT8) deposited Al₂O₃ films. A red shift of the peak position was observed after polymerization of all monomer (F(T2)₂, F(T3)₂, F(T4)₂) deposited films. The same trend was observed for polymer (pFT4, pFT6, pFT8) sensitized TiO₂ films (see the main text). These trends imply that the conjugation of the thiophene units has been extended by reaction between the neighboring molecules on the metal oxide surface, forming molecular wires, in agreement with our previous observation.¹

![Figure S2](image)

**Figure S2.** (a-c) Normalized absorption spectra of monomer (F(T2)₂, F(T3)₂, F(T4)₂) attached Al₂O₃ films (bright blue, green and red dotted line, respectively) and polymer (pFT4, pFT6 or pFT8) attached Al₂O₃ films (dark blue, green and red solid line, respectively). For electrochemical polymerization, an electrical bias was applied to the monomer attached Al₂O₃ films in acetonitrile containing 0.1 M LiClO₄ at +1.0 V vs. Ag/AgCl for 10 min. The film was subsequently undoped by applying -0.5 V vs. Ag/AgCl for 10 min.

From Table 1, we have correlated HOMO-LUMO gap energy of the monomer and the polymer with the thiophene unit numbers. Figure S3 indicates a clear linear relationship between the HOMO-LUMO gap energy and the reciprocal of the thiophene unit numbers from monomers to
polymers. This observation is similar to the one previously observed for oligothiophene numbers, where the effective conjugation length determines HOMO-LUMO gap energy.\textsuperscript{5-6} This result potentially suggests that the HOMO-LUMO gap energy of the monomer and the polymer in this study is essentially determined by the thiophene unit length (up to 8 thiophene units).

![Graph showing the correlation between HOMO-LUMO gap energies (E) and the reciprocal of the thiophene unit numbers (1/n). The dashed-dotted line is a guide to the eye.]

**Figure S3.** Correlation between HOMO-LUMO gap energies (E) and the reciprocal of the thiophene unit numbers (1/n). The dashed-dotted line is a guide to the eye.

### 3.3 Cyclic voltammetry of monomers

To determine formal oxidation potentials of monomers F(T2)2, F(T3)2 and F(T4)2, cyclic voltammetry measurements were conducted (Figure S4). Since an obvious peak at \(\sim 1.04 \text{ V}\) has been seen in control measurement, i.e. without adding monomers, the first anodic peaks appeared after 1.04 V in the voltammogram must originate from the oxidation of monomers and the
The oxidation potentials are 1.36 V, 1.34 V and 1.14 V vs. Ag/AgCl for F(T2)2, F(T3)2 and F(T4)2, respectively. It is noted that the cathodic currents for all monomers are quite small, probably owing to the high reactivity of the monomer radical, leading to the polymerization. The decrease of oxidation potentials while increasing the chain length (from F(T2)2 to F(T4)2) can be attributed to the decease of the reactivity of the corresponding cation radical.\textsuperscript{7}

**Figure S4.** Normalized cyclic voltammograms of 1 mM monomer F(T2)2 in acetonitrile/ethanol (1:1 vol\%) containing 0.1 M Bu₄NPF₆ (dark blue solid line), 1 mM monomer F(T3)2 (dark green solid line) or 1 mM F(T4)2 (dark red solid line) in acetonitrile/DMF (1:1, vol\%) containing 0.1 M Bu₄NPF₆, and 0.1 M Bu₄NPF₆ acetonitrile solution (black dotted line) as a reference. These were measured with the scan rate of 50 mVs\textsuperscript{-1}. 
3.4 Polymer (molecular wire) oxidized states

Figure S5 shows absorption difference spectra of polymer (pFT4, pFT6, pFT8) sensitized TiO$_2$ film electrode under the bias application. The spectra were obtained by subtracting the reference spectrum from the spectrum observed at the applied bias after 10 min stabilization.

Figure S5. Absorption difference spectra of pFT4 (a), pFT6 (b) and pFT8 (c) sensitized TiO$_2$ film, obtained by increasing positive applied bias. The number in the figure indicates applied bias (vs. Ag/AgCl).

3.5 Assignment of transient absorption spectra of polymer sensitized TiO$_2$ film

Figure S6 compares transient absorption spectra of polymer (pFT4, pFT6, pFT8) sensitized TiO$_2$ film with the spectra of polymer (pFT4, pFT6, pFT8) oxidized states obtained under the bias application of +0.7 V vs. Ag/AgCl into the polymer sensitized TiO$_2$ film electrode. The comparison clearly suggests that light excitation of the polymer induces an electron injection from the excited polymer to the TiO$_2$ conduction band, forming a charge separated state of an electron in the TiO$_2$ and a hole in the polymer wire.
Figure S6. Transient absorption spectra of pFT4 (a), pFT6 (b) and pFT8 (c) sensitized TiO$_2$ film (solid line), obtained at 2 $\mu$s after 390, 440 and 440 nm excitation, respectively. The oxidized state spectra of polymer (pFT4, pFT6, pFT8) sensitized TiO$_2$ film, generated by applying bias at +0.7 V vs. Ag/AgCl, are shown as dotted lines for comparison.
3.6 Transient photoconductivity decays

Figure S7 shows photoconductivity decays of (a) the monomer and (b) the polymer sensitized TiO$_2$ films, where $\Sigma\mu$ is the sum of charge carrier mobility ($\Sigma\mu = \mu_r + \mu_c$) and $\phi$ is the electron injection yield available in Table 2.

![Figure S7. Photoconductivity transients of (a) F(T2)$_2$, F(T3)$_2$ and F(T4)$_2$ and (b) pFT4, pFT6 and pFT8 sensitized TiO$_2$ films with 355 nm excitation and excitation energy density of 450 $\mu$J/cm$^2$). Solid lines indicate fits to a second-order rate equation, $\phi \Sigma\mu(t) = \phi \Sigma\mu_{max}/(1 + at)$.](image)
4. Monte Carlo simulation using Random Walk model for charge recombination

Dynamics of charge recombination between an electron in the TiO$_2$ and a hole in a monomer or polymer wire were analyzed by Monte Carlo simulation using a random walk model. Previously, a random walk model was extensively studied to understand charge recombination dynamics in dye sensitized TiO$_2$ films.$^{8-11}$ Since “diffusion” is the main driving force (entropy term in the Gibbs energy) for the electron transport inside the TiO$_2$ in dye sensitized solar cells, the random walk simulation (for an electron to randomly walk in the TiO$_2$ through multiple trapping and de-trapping) is reasonable to be employed to account for the charge recombination dynamics. In the present study, we have modified this simulation to explain the long lived charge separated states in the polymer sensitized TiO$_2$ system.

A schematic model is shown in Scheme S1. A monomer (F(T2)2) sensitized TiO$_2$ system is presented in Scheme S1d as an example. An electron is injected from the monomer to the TiO$_2$, and we consider in the model that an electron and a hole are able to individually move through states inside the TiO$_2$ and the monomer, respectively. We assume that only one electron is available and moves within a small area, i.e. intraparticle movement, since the TAS laser excitation intensity is sufficiently low (equivalent to <1 electron per TiO$_2$ nanoparticle).$^{12}$ We have restricted movement of an electron in 2 dimensional space by defining that there are 15 $\times$ 15 assembly of electron trap states (boxes) available for one injected electron to walk randomly. Note we found that the matrix of greater than 10 $\times$ 10 states resulted in the similar simulation outcome. Here, we consider one pair of electron and hole for the charge recombination simulation.
Scheme S1. (a-c) Simplified monomer and polymer models to determine a hole occupied state. A box represents a state to accept a hole. A blue box indicates the thiophene units whose energy level depends on the number of thiophene units. A white box indicates a fluorene unit. The bar underneath a box represents a link for a hole to recombine with an electron, i.e. a dipropionic acid anchoring group at the fluorene unit. (a) F(T2)2 has three boxes to accept a hole. A hole can randomly walk from a box to the next with the waiting time until a hole from the middle box recombines with an electron. (b) F(T3)2 or F(T4)2 has three boxes, however a hole can recombine from one of the side boxes (i.e. through the thiophene units attaching to the TiO2 surface) as well as from the middle box. (c) We assume a polymer wire has three white and four blue boxes, while blue and white boxes are located alternately. (d) A model example: F(T2)2 sensitized TiO2. The model consists of 15 x 15 matrix of electron trap states (boxes) in TiO2 and 3 acceptable hole states (boxes) in F(T2)2. An electron and a hole can randomly walk through their empty electron and hole boxes until they simultaneously occupy the boxes connected with the bar.
The simulation was performed with the random walk model programmed using a Microsoft Visual Basic for Applications (VBA) program compiled using Microsoft’s event-driven programming language Visual Basic 6 and its associated integrated development environment. The simulation was initiated from the initial charge separated state, i.e. a hole in the fluorene unit in the middle of the sensitizer and an electron in the top-middle box to which a dipropionic acid is attached. Once an electron is injected, the electron is allowed to move only to a next neighboring state located horizontally or vertically (randomly) after an interval, i.e. the time required for an electron to escape from the trap state (waiting time) which is dependent upon the activation energy of the site currently occupied. The waiting time, $t_e$, is provided using exponential random numbers by the following formula:\(^9\)

$$t_e = -\ln(R) \ t_{e0} \ e^{-(E_e-E_0)/kT} \quad (S1)$$

where $R$ is the random number uniformly distributed between 0 and 1, $E_e$ is the energy of the site currently occupied, $E_0$ is the energy of the lowest state through which the electron conduction occurs, i.e. the mobility edge or the electron conduction edge, $k$ is the Boltzmann constant and $T$ is the absolute temperature. In the present model, to simplify the random walk simulation and to clarify the influence of the hole movement on the recombination rate, we do not consider the distribution of electron trap state energy levels in the TiO$_2$. $t_{e0}$ is the adjustable parameter that controls the time scale of the simulation. Note that the present model does not consider a tunneling event.\(^{10-11}\)
In the present simulation, a hole can also move, but the movement is restricted in one dimensional path. Scheme S1a shows a schematic structure of F(T2)2 hole accepting states, a box represents one state to accept a hole. The middle white box represents a fluorene unit, while the thiophene units (bithiophene) are shown as a side blue box. The bar underneath the white box represents two dipropionic acid anchoring groups which can attach to the TiO₂ surface. In this simplified structure, a hole can move between a white and a blue box, however if the torsional angle between the fluorene and thiophene units is relatively large, thermal excitation is required for a hole to move to the fluorene unit owing to the difference in the potential energy level of the thiophene units compared to that of the fluorene unit.⁷ ¹³ For this hole movement, we have introduced another waiting time.

\[ t_h = -\ln(R) t_h^0 e^{(E_{th}-E_f)/kT} \]  \hspace{1cm} (S2)

where \( E_{th} \) is the potential energy of the thiophene units and \( E_f \) is the potential energy of the fluorene unit. \( t_h^0 \) is also the adjustable parameter that controls the time scale of the simulation. In the model, we assume that the charge recombination occurs via a through-bond electron transfer reaction, i.e. between a hole in the white middle box and an electron in the electron acceptor box to which a dipropionic acid is attached.

Scheme S1b shows a case of F(T3)2 or F(T4)2 attached TiO₂ system. In this case, the thiophene units (ter- or quarter- thiophene) are considered as one box, and one of the side boxes is tilted, and attaches to the TiO₂ surface, since the thiophene units are sufficiently long. Despite this surface attachment, we assumed that both thiophene units have identical potential energy level, so that the same activation energy is required for a hole to move to the fluorene unit, i.e. a
hole moves to the fluorene unit with the same waiting time defined by Equation S2. In this case, charge recombination occurs through the fluorene unit or the thiophene units attaching to the TiO$_2$ surface. We found that this additional charge recombination path (through the surface attached thiophene units) was required to explain the decay dynamics, and has reproduced the charge recombination decay, as shown in Figure 7.

As for a polymer wire attached TiO$_2$ system, the schematic structure is shown in Scheme 1c. In this case, we have modelled that a polymer has three white and four blue boxes, while blue and white boxes are located alternately. The waiting time is also applied based on Equation S2, when a hole moves between the fluorene and the thiophene units. In the simulation, we assumed charge recombination occurs through any of the fluorene unit.

The simulation completes, i.e. charge recombination occurs, when the electron and the hole simultaneously occupy the boxes which are connected by the bar in the sensitized structure (through-bond reaction). The total simulation time (equivalent to the charge separated state lifetime) was recorded from the initial charge separated state, and the simulation was repeated for 10,000 times. The distribution of the lifetimes is plotted in Figure 7, and compared to the experimental charge recombination decays.

**Table S1. Fitted hole waiting time for the results obtained from Monte Carlo simulation**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fitted hole waiting time / µs</th>
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<tbody>
<tr>
<td>TiO$_2$- F(T2)2</td>
<td>4.2</td>
</tr>
<tr>
<td>TiO$_2$- F(T3)2</td>
<td>4.2</td>
</tr>
<tr>
<td>TiO$_2$- F(T4)2</td>
<td>210</td>
</tr>
<tr>
<td>TiO$_2$-pFT4</td>
<td>340</td>
</tr>
<tr>
<td>TiO$_2$-pFT6</td>
<td>420</td>
</tr>
<tr>
<td>TiO$_2$-pFT8</td>
<td>440</td>
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</tbody>
</table>
References


