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<td>Sum, Tze Chien</td>
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The Photophysics of Perovskite Solar Cells

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ABSTRACT

Solution-processed hybrid organic-inorganic perovskite solar cells, a newcomer to the photovoltaic arena, have taken the field by storm with their extraordinary power conversion efficiencies exceeding 17%. In this paper, the photophysics and the latest findings on the carrier dynamics and charge transfer mechanisms in this new class of photovoltaic material will be examined and distilled. Some open photophysics questions will also be discussed.

Keywords: methylammonium lead iodide, perovskite solar cells, photophysics, transient optical spectroscopy, charge dynamics, Charge transfer mechanisms

1. INTRODUCTION

Organic-inorganic perovskite solar cells (or simply perovskite solar cells) is the recent major breakthrough in low-cost photovoltaics. In a matter of 5 years, these solution-processable solar cells established themselves as the forerunner amongst the 3rd generation photovoltaic technologies that include organic photovoltaics, dye sensitized solar cells and quantum dot solar cells. Although claims of power conversion efficiencies (PCEs) as high as 19.3% [1] have been reported at the recent Materials Research Society 2014 Spring meeting, the certified record PCE to date is 17.9% [2], up from a mere 3.8% [3] back in 2009. Comparatively, dye-sensitized solar cells needed more than two decades of intensive research to surpass the 10% PCE mark. Despite the phenomenal rise in device performances, a complete picture of the photophysical mechanisms in perovskite solar cells is still elusive.[4] In this paper, I will first briefly review the current progress in field of perovskite solar cells and then proceed to trace the developments in the photophysics studies. I will also highlight our findings of long range balanced electron-hole diffusion lengths, hot-hole cooling dynamics in CH3NH3PbI3 and the demonstration of amplified spontaneous emission from these materials.[5, 6] Lastly, the open questions in the photophysics of these materials will also be discussed.

2. ORGANIC-INORGANIC PEROVSKITE SOLAR CELLS

2.1 Structure of 3-Dimensional Organic-Inorganic Perovskites

Perovskite is a generic name for compounds with the common AMX₃ formula, where the A-cation is located at the eight corners of a cubic unit cell and the M-cation is surrounded by 6 X-anions in at the center of the [PbI₆]⁴⁻ octahedron – see Figure 1(a) for the case of CH₃NH₃PbI₃. Although the common name for calcium titanate (CaTiO₃) shares the same “perovskite” tag, the only relation these organic-inorganic perovskite materials (e.g., CH₃NH₃PbI₃) have with their namesake is only their structure. Prior to advancements in nanoscience in the 1980’s, this family of hybrid materials capable of forming 3-dimensional (3D) to 0-dimensional (0-D) analogs with the [PbI₆]⁴⁻ octahedron unit cell, has been investigated extensively as model systems in the study of quantum confinement effects on semiconductor mesoscopic structures. CH₃NH₃PbX₃ (where X refers to Cl, Br and I), the photovoltaic material of choice under extensive scrutiny is formed from a 3D network of [PbI₆]⁴⁻ octahedrons – Figure 1(b).

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2.2 Brief Overview of the Field and Basic Device Architectures

Photovoltaic applications of CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$ can be traced to the early works of T. Miyasaka and coworkers in 2009 who utilized them as light absorbers on mesoporous TiO$_2$ layers with halide electrolytes, yielding PCEs of ~3.81%. Subsequently, N. G. Park and coworkers optimized such liquid electrolyte perovskite solar cells to ~6.54% in 2011. However, issues with stability and the perovskite dissolving in the liquid electrolyte plague these early cells. A major breakthrough in stability and efficiency was reported by N. G. Park, M. Grätzel and coworkers in 2012, with the realization of CH$_3$NH$_3$PbI$_3$ solar cells with 9.7% PCE. This was followed by the work by H. J. Snaith, T. Miyasaka and coworkers who utilized the mixed halide CH$_3$NH$_3$PbI$_3$-Cl on both mesoporous TiO$_2$ and Al$_2$O$_3$ layers where the devices with inert mesoporous Al$_2$O$_3$ layers as supports yielded the higher efficiencies of 10.9%. This finding established the n-type semiconductor characteristics of perovskite. The ambipolar characteristics of CH$_3$NH$_3$PbI$_3$ became apparent from the work by M. Grätzel and coworkers when a respectable PCE of 5.5% was obtained for hole conductor-free perovskite solar cells (indicating p-type characteristics).

The next milestones in PCE improvements were in the middle of 2013 where M. Grätzel and coworkers achieved a PCE of 15% (and certified value of 14.1%) using a sequential deposition method to fabricate perovskite on mesoporous TiO$_2$. This was closely followed by H. J. Snaith and coworkers who fabricated planar heterojunction perovskite solar...
cells with vapor deposition and achieved 15.4% PCE. [12] A flurry of papers on improved device performances >15% soon followed (15.6% [13]; 15.7% [14]; 15.9% [15]) and eventually culminating with the certified report of 17.9% [2] in early 2014. Figure 2 aptly summarizes the most common types of perovskite solar cell device architectures – those with injecting or non-injecting mesoporous layer that are fabricated using spin coating or sequential deposition process while those of the planar heterojunction configuration that are fabricated using spin coating or vapor deposition.

3. PHOTOPHYSICS OF ORGANIC-INORGANIC PEROVSKITES

Despite the great strides made with the perovskite solar cell efficiency, a clear understanding of the fundamental photophysics in these cells is still severely lacking. To realize the full potential of these perovskite solar cells, both photophysical characterization and device optimization approaches go hand-in-hand to understand their fundamental optical and electrical properties. A wide array of optical spectroscopy techniques is available to the spectroscopist to characterize the optical properties and probe charge dynamics of these materials and devices. These range from the ubiquitous absorption spectroscopy to more sophisticated pump-probe techniques of transient absorption, terahertz spectroscopy and photoconductance spectroscopy. I will first discuss about the intrinsic properties of organic-inorganic perovskites, followed by the charge dynamics of bare perovskite films and the charge transfer mechanisms in perovskite solar cells.

3.1 Photoexcited species of Perovskite Thin Films

The workhorse photovoltaic material, CH$_3$NH$_3$PbI$_3$ possesses large absorption coefficient of $1 \times 10^5$ cm$^{-1}$ (at 500 nm wavelength) [5] and fairly large exciton binding energy ($E_b$ comparable to larger than room temperature thermal energies of $k_B T \sim 25$ meV) – see table 1 below. Techniques ranging from optical absorption [16] and magneto-absorption [17, 18] as well as from temperature-dependent photoluminescence (PL) [19-21] and temperature-dependent absorption spectroscopy [22] have been used to estimate $E_b$. The excitons in CH$_3$NH$_3$PbI$_3$ belong to the more delocalized Wannier-type with exciton Bohr radius, $r_B \sim 30$ Å.[16, 23] The larger binding energies for CH$_3$NH$_3$PbBr$_3$ and the mixed halide CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ system indicates a more tightly bound nature of the excitons resulting from the halogen substitution. The value of perovskite $E_b$ is of significance in photovoltaics because it hints at whether the fundamental excited species following photoexcitation could exist as free carriers or bound electron-hole pairs requiring further dissociation. This has important bearings on the subsequent charge extraction mechanisms (i.e., are we transporting energy or charge?) and the device architecture (i.e., is an interface needed to split the exciton?).

Table 1. Exciton binding energies $E_b$ of CH$_3$NH$_3$PbI$_3$, CH$_3$NH$_3$PbBr$_3$, and CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskites

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<tr>
<th>Compound</th>
<th>$E_b$ (meV)</th>
<th>Experimental Method</th>
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<tr>
<td>CH$_3$NH$_3$PbI$_3$</td>
<td>30</td>
<td>optical absorption[16]</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>magneto-absorption[17]</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>temperature dependent PL[19]</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>magneto-absorption[18]</td>
</tr>
<tr>
<td></td>
<td>19±3</td>
<td>temperature dependent PL[20]</td>
</tr>
<tr>
<td></td>
<td>32±5</td>
<td>temperature dependent PL[21]</td>
</tr>
<tr>
<td>CH$_3$NH$_3$PbBr$_3$</td>
<td>76</td>
<td>magneto-absorption[18]</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>optical absorption[16]</td>
</tr>
<tr>
<td>CH$_3$NH$<em>3$PbI$</em>{3-x}$Cl$_x$</td>
<td>98</td>
<td>temperature dependent PL[24]</td>
</tr>
<tr>
<td></td>
<td>55±20</td>
<td>temperature dependent absorption[22]</td>
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There have been several works on elucidating whether the primary photoexcited species are excitons or free carriers perovskites in CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite solar cells.[22, 25] V. Sundström and coworkers utilized time-resolved terahertz spectroscopy to uncover evidence of the electron-hole pairs dissociating to form highly mobile charges in CH$_3$NH$_3$PbI$_3$ within 2 ps following photoexcitation. [25] A. Petrozza and coworkers, on the other hand investigated the exciton binding energy of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ using temperature dependent absorption and through
Based on these reports, T. C. Sum in collaboration with N. Mathews and coworkers [5] devised quenching experiments utilizing femtosecond transient optical spectroscopy (time-resolved photoluminescence and transient absorption) of CH$_3$NH$_3$PbI$_3$ heterojunctions with selective electron or hole extraction to decouple the electron and hole dynamics in this material – see Figure 3(a) and (b). Using a diffusion model with conservative approximations, our findings revealed clear evidence of balanced and long-range electron-hole diffusion lengths of at least 100 nm in solution-processed CH$_3$NH$_3$PbI$_3$ (Figure 3(c)). Concurrently, using the same PL quenching approach, H. J. Snaith and coworkers’ [28] findings on the electron-hole diffusion lengths in CH$_3$NH$_3$PbI$_3$ concur with ours. Additionally, they reported diffusion lengths one order longer (i.e., >1 μm) than CH$_3$NH$_3$PbI$_3$ in the mixed halide CH$_3$NH$_3$PbI$_3$Cl$_x$, although no clear reason was identified for this difference. However, a recent work by V. Sundström and coworkers using time-resolved numerical simulations of the fraction of free charges vs excitons show that exciton population undergoes full dissociation under photovoltaic device operating conditions. [22] However, a recent study [21] by V. Sundström and coworkers found that the exciton dissociation in CH$_3$NH$_3$PbI$_3$ are temperature activated and is <100% efficient at room temperature. Our understanding of the initial photoexcitation mechanism is still far from complete, further studies on the on the dynamic interplay and interactions between the exciton and the free charge populations in existing and newer perovskite systems (e.g., HC(NH$_2$)$_2$PbI$_3$ and CH$_3$NH$_3$SnI$_3$) are warranted.

3.2 Long range and balanced electron-hole diffusion lengths of perovskite thin films

Indications of ambipolar charge transport in perovskites become apparent by 2013 when efficient perovskite-based devices in a broad range of device architectures are reported. As an absorber layer (i.e., thin perovskite layer sandwiched between a mesoporous TiO$_2$ photoanode and a hole-transporting material (HTM) layer (i.e., Spiro-OMeTAD)), perovskite performs well [8, 26]. The demonstration of perovskite solar cells fabricated with an insulating Al$_2$O$_3$ scaffold instead of the TiO$_2$ photoanode shows that perovskite can also function well as both an absorber and an electron transporter. [27] Lastly, HTM-free perovskite solar cells shows that perovskite can also work as an absorber and a hole transporter. [9]
microwave conductivity to monitor the photoconductance kinetics of the charges [21] instead of the photoluminescence decays of the luminescent species, found that the diffusion lengths of photoinduced carriers in CH$_3$NH$_3$PbI$_3$ can exceed 5μm. H. J. Snaith and coworkers also investigated the HC(NH$_2$)$_2$PbI$_3$ system (where the methylammonium cation is replaced by the larger formamidinium cation) and found that although their electron and hole diffusion lengths are long (few hundred nm), they are not balanced in HC(NH$_2$)$_2$PbI$_3$ even though device efficiencies of ~14% was reported. [29] Although the balanced nature may be unique to the CH$_3$NH$_3$PbX$_3$ systems, all these works nonetheless show that the electron-hole diffusion lengths in perovskites are indeed much longer than the typically ~10 nm distances for most solution processed materials. The long diffusion lengths allow charges to be extracted before they recombine; thereby permitting high efficiencies in these perovskite solar cells.

L. M. Herz in collaboration with H. J. Snaith and coworkers [30] utilized transient THz spectroscopy to investigate the origins of the long electron-hole diffusion lengths in CH$_3$NH$_3$PbI$_3$Cl$_x$ and CH$_3$NH$_3$PbI$_3$ and to elucidate their charge carrier mobilities. Their findings reveal that both the monomolecular (first order, i.e., from geminate recombination of excitons and/or from trap- or impurity-assisted recombination) and bimolecular (second order) charge carrier recombination rates are extremely low, with the latter slower than the calculated Langevin limit by at least four orders of magnitude. However, the Auger (third order) recombination rates, were found to be high ~10$^{-29}$ cm$^6$s$^{-1}$ – a value which is 2 orders larger than highly-doped bulk Si wafers; [31] while yet comparable to strongly confined colloidal quantum dots. [32] The lower bound values of the charge carrier mobilities for CH$_3$NH$_3$PbI$_3$Cl$_x$ and CH$_3$NH$_3$PbI$_3$ were determined to be 11.6 cm$^2$V$^{-1}$s$^{-1}$ and ~8 cm$^2$V$^{-1}$s$^{-1}$, respectively, which are extremely high for the solution-processed perovskites and are comparatively >20 times larger than that of mesoporous TiO$_2$. The origins of the long electron-hole diffusion lengths stem from the exotic combination of low charge carrier recombination rates and high charge carrier mobilities in these perovskites. These findings concur with a recent study [21] by V. Sundström and coworkers who extended the work to examine the effects of temperature on the exciton dissociation and recombination and carrier mobility in CH$_3$NH$_3$PbI$_3$ thin films using photoluminescence spectroscopy and transient microwave photoconductance spectroscopy. They found that the charge carrier mobility is very high (>6.2 cm$^2$V$^{-1}$s$^{-1}$) at room temperature and increases as temperature is decreased due to suppression of phonon scattering. In addition, their work shed some light on the much lower bimolecular recombination rates (at least 2 orders lower) compared to the calculated Langevin limit – a 75 meV activation energy is needed to initiate 2$^{nd}$ order charge recombination in perovskite. Detailed understanding of these fundamental photophysical processes is essential for optimizing new perovskite materials for photovoltaic applications.

3.3 Hot-hole cooling, multi-particle processes, amplified spontaneous emission and lasing from perovskite thin films

T. C. Sum in collaboration with N. Mathews and coworkers [5] examined the early time carrier dynamics in the CH$_3$NH$_3$PbI$_3$ system. Femtosecond TAS measurements with selective 400 nm and 600 nm pump excitation (fluence <1.3 μJ/cm$^2$) and WLC probe uncovered a slow 0.4 ps hot hole cooling process from a deeper level VB2 (below the valence band edge (VB1)) to VB1 – see Figure 4(a), (b) and (c). It is therefore possible to tailor the energy levels of the HTM to permit efficient extraction of these hot hole energies before they cool down to VB1. Potentially, this could be leveraged exceed the theoretical Shockley-Queisser limit.[33] Further investigations into this area should be conducted. It is important to note that the carrier dynamics in the perovskite system are strongly pump fluence dependent due to their large light absorption coefficients and the long charge diffusion lengths. Careful control of the pump fluence in ultrafast optical spectroscopy of perovskites is absolutely essential in studying their intrinsic photophysical properties. Multi-particle Auger (third order) recombination processes becomes dominant for pump fluence >2.6 μJ/cm$^2$. In fact, we recently discovered that at pump fluence >12 μJ/cm$^2$, amplified spontaneous emission (ASE) prevails and even out-competes the Auger processes [6] – possibly through electron-hole plasma permitting optical gain to occur. The low threshold ASE stems from large absorption coefficients, low bulk defect densities and relatively slower Auger recombination. Through time- and excitation-energy dependent photoluminescence spectroscopy, L. M. Herz and coworkers show that CH$_3$NH$_3$PbI$_3$Cl$_x$ exhibit emission linewidth broadening suitable for the amplification of femtosecond pulses [34], further supporting our observations. Nevertheless, our demonstration of optical gain, wavelength tunable amplified spontaneous emission (see Figure 4(d)) from perovskite thin films and lasing from naturally formed perovskite crystals [6] exemplify the notion that a good solar cell is also a good light emitter. [35] Using a distributed Bragg reflector (DBR), lasing [36] was also demonstrated by H. J. Snaith in collaboration with R. H. Friend and coworkers – see Figure 4(e). Thus, the photoluminescence or more specifically, the electrical luminance quantum efficiency in devices could be a key indicator for optimizing new perovskite materials.
Figure 4. Normalized bleaching kinetics at 480 and 760 nm in a short time range show the intervalence band hot hole cooling for CH$_3$NH$_3$PbI$_3$ film (in vacuum) after excitation at (a) 400 nm (1 $\mu$J/cm$^2$) and (b) 600 nm (1.3 $\mu$J/cm$^2$). (c) A schematic illustrating the hot-hole cooling and charge recombination within CH$_3$NH$_3$PbI$_3$ and charge separation at the CH$_3$NH$_3$PbI$_3$/PCBM and CH$_3$NH$_3$PbI$_3$/Spiro-OMeTAD interfaces. The approximate positions of VB1 and VB2 were obtained from the TA measurements. (d) Wide wavelength tunability of ASE wavelengths from low-temperature solution-processed organic–inorganic halide perovskite films fabricated by mixing the precursor solutions. (e) Emission spectrum of a vertical microcavity with the structure as shown in the inset using a perovskite film as the gain medium. The thickness of the perovskite layer was around 500 nm, and it was around 1 $\mu$m for the PMMA layer. Excitation was performed with a pulsed laser (400 ps) at 2.33 eV and fluences as stated. At low fluences, three modes are resonant in the cavity with a mode spacing of $\sim$9.5 THz. At sufficiently high fluences, the mode at 1.6 eV is amplified. (a), (b) and (c) are reproduced with permission from ref. [5], Copyright 2013, Science (AAAS). (d) is reproduced with permission from ref. [6], Copyright 2014, Nature Publishing Group. (f) is reprinted (adapted) with permission from ref. [36], Copyright 2014, American Chemical Society.

### 3.4 Summary of Photophysical Processes in perovskite thin films

Figure 5 shows a generalized scheme of the dynamic interplay of the various photophysical processes and relaxation mechanisms in bare CH$_3$NH$_3$PbI$_3$ or CH$_3$NH$_3$PbI$_{1-x}$Cl$_x$ perovskite thin films. Following photoexcitation at low light intensities, electron-hole pairs generated will rapidly form highly delocalized Wannier excitons. With their binding energies comparable to the room temperature thermal energies, spontaneous dissociation of the excitons would occur – leading to a coexistence of excitons and free carrier populations in the bare films. Monomolecular (or 1$^{st}$ order) recombination processes such as bound electron-hole pair (or geminate) recombination and trap-assisted recombination are found to be insignificant. [37] At stronger light intensities, bimolecular (or 2$^{nd}$ order) recombination processes like the recombination between a free electron and a free hole (or non-geminate) recombination is also extremely low with at least 2-4 orders lower compared to the calculated Langevin recombination. [21, 37] The multiparticle (3$^{rd}$ order) Auger recombination process is dominant but eventually loses out to ASE/lasing at even higher pump fluences, [5, 6] with optical gain possibly from electron-hole plasma formation. Nevertheless, in bare perovskite films and without charge extraction, the photoexcited species (excitons and free carriers) undergo radiative (luminescence) or non-radiative
processes within the perovskite. Typically, under solar light intensities (low intensity excitation), Auger recombination or ASE would be strongly suppressed. With the non-radiative pathways (geminate recombination, trap-assisted recombination and Auger recombination) weak or inactive under solar light intensities, it is therefore understandable that these perovskites make excellent photovoltaic and light emitting materials.

![Diagram of photophysical processes and loss mechanisms in perovskites following photoexcitation.](image)

**Figure 5.** A schematic of the photophysical processes and loss mechanisms in perovskites following photoexcitation. Efficient paths (black lines) and suppressed paths (grey lines). Monomolecular recombination is charge carrier density independent, while bi-molecular and Auger recombination are charge carrier density dependent processes that would typically be present under strong photoexcitation. In fact, under even higher photoexcitation densities, amplified spontaneous emission (ASE) will out-compete Auger recombination. However, under solar light intensities (weak excitation), these latter processes will be strongly suppressed. Figure reproduced with permission from ref. [4] Copyright 2014, Royal Society of Chemistry.

### 4. CHARGE TRANSFER MECHANISMS IN PEROVSKITE SOLAR CELLS

The earliest study on the dynamics of the charge separation processes in CH$_3$NH$_3$PbI$_3$/TiO$_2$ solar cells probed using femtosecond transient absorption spectroscopy (fs-TAS) can be found in the 2012 groundbreaking paper on perovskite solar cells by N. G. Park in collaboration with M. Grätzel and coworkers. [8] However, clear evidence of efficient electron injection into TiO$_2$ could not be observed in that work – attributed to overlapping signals from the stimulated emission from the perovskite. This shortcoming was resolved in early 2014 in the work by J.-E. Moser in collaboration with M. Grätzel and coworkers, who elucidated the mechanism of the charge transfer processes in perovskite solar cells (Figure 5(a)). By probing in the infrared (1.4 μm), direct observation of only the carrier’s population decay within the perovskite itself is now possible (Figure 5(b)), thus averting the spectral overlap encountered in the earlier study. [8] Clear evidence of both electron (or hole) injection from the photoexcited CH$_3$NH$_3$PbI$_3$ into TiO$_2$ (or the HTM (spiro-OMeTAD)) occurring simultaneously over comparable ultrafast timescales (≤ 3ps) were presented.[38]
Presently, the questions on: (i) whether electron collection is more efficient through the mesoporous TiO$_2$ or within the perovskite itself; and (ii) which pathway results in higher device efficiency in perovskite solar cells remain open. Using transient photocurrent measurements, H. J. Snaith in collaboration with T. N. Murakami and T. Miyaska and coworkers showed that the charge collection in the insulating Al$_2$O$_3$-based devices is faster than the TiO$_2$-based devices – indicating the perovskite material itself is more efficient in transporting negative charge than the mesoporous TiO$_2$.[27] This is further supported in a very recent work [25] by V. Sundström and coworkers using time-resolved terahertz spectroscopy where they found that although charge injection into mesoporous TiO$_2$ is efficient, the charge mobility in CH$_3$NH$_3$PbI$_3$/TiO$_2$ is 3-4 times slower than in neat CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbI$_3$/Al$_2$O$_3$, which could lead to unbalanced charge transport – see Figure 5(d). On the other hand, Marchioro et. al.’s findings [38] showed that it is advantages to use TiO$_2$ as the electron acceptor and transporter, together with HTM in perovskite solar cells. In that work, transient absorption spectroscopy showed that the amount of long-lived charges in the TiO$_2$/CH$_3$NH$_3$PbI$_3$/HTM samples is higher than that in the Al$_2$O$_3$/CH$_3$NH$_3$PbI$_3$/HTM samples (Figure 5(b)) – indicating a more efficient charge separation in the former. Furthermore, charge recombination with oxidized HTM species was also found to be slower on TiO$_2$ films compared to Al$_2$O$_3$ films (Figure 5(c)). The answer to these questions maybe non-trivial as the efficiency of charge extraction in a perovskite solar cell also depends on the ratio between charge recombination and charge separation rates. Further investigations of the interfacial charge dynamics and spectroscopic measurements in working solar cells at different applied voltages are urgently needed.

Figure 6: (a) Schematic diagram of energy levels and electron transfer processes in an HTM/perovskite/TiO$_2$ cell. (1): Electron Injection; (2): Hole injection; (3): Radiative exciton recombination; (4) Non-radiative exciton recombination; (5) Back electron transfer at the TiO$_2$ surface; (6) Back charge transfer at the HTM surface; (7) Charge recombination at the TiO$_2$/HTM interface. (b) Transient absorption signals were measured at a probe wavelength of 1.4 μm following femtosecond- laser pulsed excitation at 580 nm: CH$_3$NH$_3$PbI$_3$ on TiO$_2$ (black); CH$_3$NH$_3$PbI$_3$ on Al$_2$O$_3$ (blue); CH$_3$NH$_3$PbI$_3$ and spiro-OMeTAD on TiO$_2$ (red); CH$_3$NH$_3$PbI$_3$ and spiro-OMeTAD on Al$_2$O$_3$ (green). Thick solid lines represent bi-exponential fits of experimental points starting at t = 1 ps. A$_2$ represents the normalized absorbance change at 25 ps, used as a metric to compare the various samples. (c) Samples with HTM. Signals mainly reflect the decay of the h$^+$ (HTM) population. CH$_3$NH$_3$PbI$_3$ and spiro-OMeTAD on TiO$_2$ (red); CH$_3$NH$_3$PbI$_3$ and spiro-OMeTAD on Al$_2$O$_3$ (green). Thick lines represent stretched exponential fit of data. (d) Early time dynamics of neat CH$_3$NH$_3$PbI$_3$ (black), CH$_3$NH$_3$PbI$_3$/Al$_2$O$_3$ (red), and CH$_3$NH$_3$PbI$_3$/TiO$_2$ (green). Dissociation of excitons to free carriers manifest as the ~2 ps rise in the THz kinetics of neat CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbI$_3$/Al$_2$O$_3$. Figure (a) – (c) is reproduced with permission from ref. [38], Copyright 2014, Nature Publishing Group. Figure (d) is reprinted (adapted) with permission from ref. [25], Copyright 2014, American Chemical Society.
5. CONCLUSIONS AND FUTURE OUTLOOK

Organic-inorganic perovskites are indeed a novel class of materials with remarkable light harvesting properties. Despite the promising high efficiencies demonstrated in this low-cost solution-processable system, major hurdles to practical application include the presence of Pb in all the high performing cells; and the rapid device degradation upon exposure to moisture and ultraviolet radiation. As this field rapidly matures, large improvements to the PCE would be harder to come by. Thus the need to fully understand the photophysics becomes increasing important for further optimization. Ultrafast optical spectroscopy techniques remain the main probes of carrier dynamics and charge recombination in such photophysics studies. Apart from transient absorption spectroscopy, time-resolved optical pump-terahertz probe spectroscopy would also be extremely useful to monitor the early time excitons and free-carrier dynamics and populations in pristine films and heterojunctions. These studies could be extended with transient microwave photoconductance measurements over longer time scales for correlation with device properties. Pump-push probe, double excitation spectroscopy can be used to study the higher lying electronic states and their roles in the charge transfer. Field modulation techniques like field assisted pump-probe spectroscopy could also lead to new insights on the interplay of the exciton dissociation and the free carrier dynamics on the charge transfer under device conditions.

In these crystalline perovskite cells, the morphology, film coverage and wettability are strongly affected by the preparation approach (e.g., single precursor spin-coating; sequential deposition; or thermal evaporation). Such factors have a profound influence on the carrier dynamics and the subsequent device performance. Systematic ultrafast optical spectroscopy studies into interfacial charge transfer dynamics of perovskites prepared using various methods in thin films and in devices (under operating conditions) are urgently needed to understand the charge transfer mechanisms. Given that perovskites can undergo temperature dependent phase transitions (e.g., CH$_3$NH$_3$PbI$_3$ undergoes a tetragonal to cubic phase transition at ~327K (or ~54 °C) [39, 40]), it is also important to investigate the effects of temperature on the carrier dynamics close to such transitions (especially those near the device operating temperatures under direct sunlight). As more groups participate in the studies, the open questions on: (i) the dynamic interplay and interactions between the excitons and the free charge population and their effects on the charge separation, recombination and transport; (ii) the interfacial charge dynamics and the mechanism of the charge injection at the perovskite/mesoporous TiO$_2$; perovskite/semiconductor nanostructure; and perovskite/graphene interfaces; and (iii) the exact role of higher lying states (if any) for charge separation will eventually be addressed. The knowledge gained from the photophysical studies would be a feedback for further optimization of the newer perovskite derivatives (e.g., HC(NH$_2$)$_2$PbI$_3$, CH$_3$NH$_3$SnI$_3$) being developed. Understanding the structure-function relations through ultrafast optical spectroscopy holds the key to the development of optimal perovskite solar cells with efficiencies that could surpass the 20% target.

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