Interface-Assisted Perovskite Modulations for High- Performance Light-Emitting Diodes

Chaoyang Kuang

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Linköping 2021

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The illustration of the cover represents the perovskite light-emitting diodes designed by Chaoyang Kuang.

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During the course of the research underlying this thesis, Chaoyang Kuang was enrolled in Agora Materiae, a multidisciplinary doctoral program at Linköping University, Sweden

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千淘万漉虽辛苦，吹尽黄沙始到金。

——刘禹锡《浪淘沙·其八》

Abstract

Metal halide perovskites have emerged as a class of promising materials for a wide range of optoelectronic devices. Compared with traditional inorganic and organic semiconductors, perovskite materials can be easily processed *via* solution-based techniques at low temperatures and exhibit high photoluminescence efficiency, outstanding colour purity, and superior charge transport properties, showing great promise for cost-effective and high-performance light-emitting diodes (LEDs).

Since the first demonstration of room-temperature operating perovskite-based LEDs (PeLEDs) in 2014, various useful strategies on optimizing perovskite emissive materials and device structures have been developed, leading to notably enhanced device performance of PeLEDs during the last several years. Nevertheless, despite rapid progress in improving the external quantum efficiencies (EQEs) of PeLEDs, which are now approaching those of commercialized technologies, the operational stability of state-of-the-art PeLEDs remains poor, presenting a critical challenge for their practical applications and commercialization. Besides, a majority of the optimization strategies demonstrated for PeLEDs derive from those developed for either perovskite photovoltaics or prevailing light-emitting technologies, e.g., organic- and quantum-dot-based LEDs. Although these strategies are helpful, more comprehensive investigations and in-depth understanding of factors affecting the property of perovskite emissive layers and the device performance of ensuing PeLEDs are highly desirable to foster further advancements of this promising technology.

In this thesis, we focus our study on near-infrared PeLEDs based on triiodide perovskite emissive layers processed from precursor solutions. We systematically investigate the critical effects of precursors, substrates, and additives on the film quality of perovskite emissive layers. With the in-depth understanding of the perovskite crystallization process, we developed a range of effective interface-assisted strategies on modulating the perovskite emissive layers, which enable us to achieve PeLEDs with high EQEs and excellent long-term operational stability beyond the state-of-the-art.

In the first study, we unveiled the synergistic effect of precursor stoichiometry and interfacial reactions for PeLEDs. We reveal that ZnO efficiently deprotonates the organic cations, which promotes the formation of highly emissive perovskites from precursor solution with excess organic components, leading to the achievement of PeLEDs with a high EQE of 19.6 %. In the second study, we presented that such ZnO deprotonation process of excess organic cations can also assist the cation exchange process between cesium-formamidinium (FA-Cs)

cation exchange, enabling low-temperature fabrication of pure-phase Cs-FA mixed cation perovskite films with widely tunable emissions peaking between 715 nm and 800 nm as well as high-performance devices with peak EQEs over 15%.

In spite of enhanced device efficiency realized by the perovskite crystallization modulation, this ZnO deprotonation process places a detrimental effect on the stability of the PeLEDs, which can be accelerated by Joule heating and high electric fields during the device operation. In the third study, we, therefore, demonstrated the role of ZnO in catalyzing an efficient amidation reaction between incorporated dicarboxylic acid additives and excess FAI, preventing the above-mentioned harmful interfacial reaction. With this strategy, the operational half lifetime of the resulting PeLEDs was improved to 682 hours at 20 mA/cm² while maintaining a high device efficiency of 18.6%.

In the last work, we emphasized that the rational design of molecular reactions between two additives (diamine and triacrylate) and perovskite components with the assistance of ZnO substrates can subsequently eliminate the negative effect introduced by additive, reduce the defect density and enhance the crystal orientation in the perovskite emissive layers. The rational understanding of interfacial interactions between perovskite, additives, and ZnO, enabled us to achieve PeLEDs with a device efficiency of 23.8% as well as an outstanding operational stability T₇₀ (reduction to 70% of initial efficiency) lifetime of 290 hours at 20 mA/cm².

The study in this thesis developed effective interface-assisted modulation strategies for high-quality perovskites towards highly efficient and stable PeLEDs for commercialization. A thorough understanding of perovskite chemistry-property-performance modulation assisted by interfaces is indispensable for the future development of PeLEDs and our study took an important step.

Keywords: metal halide perovskite, light-emitting diodes, deprotonation, interfacial reaction, additive, molecular interactions.

Populärvetenskaplig sammanfattning

Metall-halid-perovskiter har visat sig vara en lovande kategori av material för en bred variation av optoelektroniska komponenter med utmärkt prestanda. Jämfört med traditionella oorganiska och organiska halvledare kan perovskit-material enkelt tillverkas och bearbetas med hjälp av lösningsbaserade tekniker vid låga temperaturer samtidigt som de visar hög fotoluminescenseffektivitet, enastående färgrenhet och överlägsna egenskaper gällande laddningstransport. Metall-halid-perovskiter uppvisar därmed stora fördelar för att kunna uppnå kostnadseffektiva och högpresterande lysdioder (LED:er).

De första perovskit-baserade lysdioderna (PeLED:er) som kunde drivas under rumstemperaturförhållanden visades upp år 2014. Sedan dess har en rad användbara strategier utvecklats för att optimera de ljusemitterande perovskit-materialen såväl som diodstrukturerna, vilket lett till märkbart förbättrad prestanda för PeLEDs. Trots snabba framsteg gällandes förbättringen av PeLED:ernas externa kvanteffektivitet, som nu närmar sig kommersiell teknik, är den operativa stabiliteten hos vetenskapens bästa PeLED:er fortfarande dålig, och utgör ett avgörande hinder och en utmaning för att nå praktiska tillämpningar och kommersialisering. En majoritet av de optimeringsstrategier som använts för PeLEDs kommer antingen från strategier som utvecklats för perovskit-solceller eller nuvarande ljusemitterande teknik, t.ex. organiska och kvantprickbaserade lysdioder (OLEDs och QLEDs). Även om dessa strategier är hjälpsamma, så är omfattande undersökningar och djupgående förståelse av faktorer som påverkar egenskaper hos det emitterande perovskitlagret och prestandan av kommande PeLED:er mycket önskvärd för att främja ytterligare framsteg av denna lovande teknik.

I denna avhandling fokuserar vi vår studie på nära infraröda peLED:er baserade på emitterande trijodid-perovskitfilmer tillverkade från prekursorlösningar. Vi undersöker systematiskt de avgörande effekterna som prekursorer, substrat och tillsatser har på filmkvaliteten hos de emitterande perovskitfilmerna. Med den djupgående förståelsen av perovskitkristalliseringsprocessen utvecklade vi en rad användbara gränssyteassisterade strategier för att modulera de emitterande perovskitfilmerna. Detta gör det möjligt för oss att uppnå PeLED:er med integrerade höga EQE:er och utmärkt långsiktig operativ stabilitet som är bättre än dagens bästa PeLED:er.

I den första studien visar vi på den nyckelroll som det alkaliska ZnO-mellanlagret har gällandes påverkan av kristalliseringen av perovskiter, så väl som det stökiometrisk förhållandet i prekursorlösningarna. ZnO kan enkelt deprotonera organiska katjoner och eliminera överskottet av FAI, vilket bidrar till en effektiv fasövergång från prekursorer till rena perovskiter med hög emissivitet

vilket leder till hög-effektivitets-dioder på 19,6 %. I uppföljningsstudien visade vi att ZnO-deprotonerings-processen av överskott av organiska katjoner också kan initiera; Cs-FA katjonutbyte, förändra legeringsförhållandt mellan Cs och FA, bilda ren-fas-Cs-FA-perovskitfilmer med justerbara emissionstoppar mellan 715 nm och 800 nm samt EQE-värden över 15% för de bästa dioderna.

Trots den förbättrade effektivitet som uppnås genom perovskitkristalliserings-moduleringen, bildar denna ZnO-deprotoneringsprocess en skadlig effekt på PeLED:ernas stabilitet. En sådan effekt kan påskyndas av Joule-uppvärmning och hög elektrisk fältstyrka under drift. I den tredje studien visade vi ZnO-katalysatorernas viktiga roll när det gäller att införa en effektiv amidiseringsreaktion mellan dikarboxylsyra-tillsatser och överskotts-FAI, vilket förhindrar ovannämnda skadliga gränsytareaktion. Med denna strategi förbättrades peLED:ers operativa halveringstid till nästan 700 timmar vid 20 mA/cm² samtidigt som en hög effektivitet på 18,6% uppehålls.

I det sista arbetet visade vi att kombinationen av två tillsatsämnen (diamin och triakrylat) kan förbättra interaktionerna mellan perovskit och tillsatser avsevärt, till exempel via tvärbinding av tillsatser och omvandling av överskott av FAI till stabila stora molekyler med hjälp av ZnO-katalysatorer. På detta vis uppnår vi flera funktioner, alltifrån passivering av defekter till perovskitkristallorienterings-reglering. Den rationella förståelsen av gränsyte-interaktioner mellan perovskit, tillsatser och ZnO, gjorde det möjligt för oss att uppnå PeLED:er med en effektivitet på 23,8% samt en enastående driftsstabilitet, med en T₇₀ livslängd på 290 timmar (med en minskning till 70% av den ursprungliga effektiviteten).

Studien som presenteras i denna avhandling visar på en effektiv strategi för att åstadkomma högeffektiva och stabila PeLED:er för framtida kommersialisering. En omfattande förståelse av kemi-struktur-egenskap-prestanda-modulering av perovskiter som assisteras av gränsytor är oumbärlig för utvecklingen av PeLED:er, och vår studie tog ett viktigt steg för den förståelsen.

Nyckelord: metall-halid-perovskiter, lysdioder, deprotonering, gränsytegenererade reaktion, tillsatsämnen, molekylära interaktioner.

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List of Publications

Papers appended in this thesis

1. Unveiling the Synergistic Effect of Precursor Stoichiometry and Interfacial Reactions for Perovskite Light-emitting Diodes

Zhongcheng Yuan, Yanfeng Miao, Zhangjun Hu, Weidong Xu, Chaoyang Kuang, Kang Pan, Pinlei Liu, Jingya Lai, Baoquan Sun, Jianpu Wang, Sai Bai, and Feng Gao. *Nat. Comm.*, 2019, 10, 2818.

Contribution: I optimized the synthesis of ZnO and contributed to the device fabrication.

2. High-performance near-infrared perovskite light-emitting diodes with fine-tuning emissions

Zhongcheng Yuan, Chaoyang Kuang, Ingemar Persson, Weidong Xu, Zhangjun Hu, Per Persson, Sai Bai, and Feng Gao
In manuscript, 2021.

Contribution: I optimized the synthesis of ZnO, contributed to the device fabrication, performed FTIR characterization.

3. Critical role of additive-induced molecular interaction on the operational stability of perovskite light-emitting diodes

Chaoyang Kuang, Zhangjun Hu, Zhongcheng Yuan, Kaichuan Wen, Jian Qing, Libor Kobera, Sabina Abbrent, Jiri Brus, Chunyang Yin, Heyong Wang, Weidong Xu, Jianpu Wang, Sai Bai, Feng Gao.
Joule, 2021, 5, 618.

Contribution: I fabricated devices and performed most of the film and device characterizations. I wrote the first draft and contributed to the final editing of the manuscript.

4. Rational design of in-situ molecular reactions for highly efficient and stable perovskite light emitting diodes

Chaoyang Kuang, Chunyang Yin, Zhongcheng Yuan, Xinyi Cai, Heyong Wang, Rui Zhang, Yu Wang, Zhangjun Hu, Sai Bai, and Feng Gao.
In manuscript, 2021.

Contribution: I fabricated devices and performed most of characterizations and data analysis. I wrote the first draft and contributed to the final editing of the manuscript.

Papers not included in this thesis

- 1. High-Quality Ruddlesden-Popper Perovskite Films Based on in-situ Formed Organic Spacer Cations**
Jian Qin, Chaoyang Kuang, Heyong Wang, Yuming Wang, Xiao-Ke Liu, Sai Bai, Mingjie Li, Tze Chien Sum, Zhangjun Hu, Wenjing Zhang, and Feng Gao.
Adv. Mater., 2019, 31, 1904243.
Contribution: I optimized the synthesis of ZnO and contributed to the device fabrication. I helped with the manuscript revision.
- 2. Ternary CuZnS Nanocrystals: Synthesis, Characterization, and Interfacial Application in Perovskite Solar Cells**
Jiangsheng Li, Chaoyang Kuang (co-first author), Min Zhao, Chengjie Zhao, Le Liu, Fushen Lu, Ning Wang, Chang-shui Huang, Chenghao Duan, Hongmei Jian, Lili Yao, and Tonggang Jiu.
Inorg. Chem., 2018, 57, 8375.
Contribution: I optimized the synthesis of CuZnS nanocrystals and contributed to most of characterization.
- 3. Dynamic Redistribution of Mobile Ions in Perovskite Light-Emitting Diodes**
Heyong Wang, Zhan Chen, Jingcong Hu, Hongling Yu, Chaoyang Kuang, Jiajun Qin, Xianjie Liu, Yue Lu, Mats Fahlman, Lintao Hou, Xiao-Ke Liu, and Feng Gao.
Adv. Funct. Mater., 2021, 31, 2007596.
Contribution: I optimized the synthesis of ZnO.
- 4. High-brightness and efficient pure-green perovskite light-emitting diodes based on FAPbBr₃ nanocrystals with short-conjugated ligands**
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- 5. Solution-processed PdCdS nanocrystals as a novel hole transport material for inverted CH₃NH₃PbI₃ perovskite solar cells**
Chenghao Duan, Min Zhao, Chaoyang Kuang (co-first author), Chengjie Zhao, Tonggang Jiu and Fushen Lu. *Sol. Energy*, 2021, 216, 321-328.
Contribution: I contributed to the data analysis and manuscript writing.
- 6. Ultra-high vacuum annealing-assisted quantum wells dimensional tailoring for perovskite light-emitting diodes efficiency enhancement**
Yong Yu, Heyong Wang, Weidong Xu, Chaoyang Kuang, Fuxiang Ji, Slawomir Braun, Xianjie Liu, Chang Yi, Feng Gao, and Mats Fahlman.
ACS Appl. Mater. Interfaces, 2020, 12, 24965.
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Part I

Background

1

Introduction

In this chapter, we will present background information and motivation of the work included in this thesis. The goal of this study is to achieve high-efficiency and stable perovskite light-emitting diodes, through a range of interface-assisted modulation strategies of perovskite emissive layers. Details about the thesis structure will also be included.

Contents

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1.1 Lighting and display

Light exists ubiquitously in our daily life and provides human beings with brightness and warmth. Although it took more than millions of years for us to get to know, utilize, improve, and finally produce light, such journey witnesses the booming human civilization. Lots of progress have been achieved in light

generation, especially in discovering luminescent materials and inventing new light-emitting devices or setups. In the early history of human beings, the only approach to generate light is to burn things and typical examples are torches, candles, and oil lamps.

The discovery of electricity by Benjamin Franklin (with his famous kite experiment) brought new opportunities for novel lighting devices. With the contributions from Joseph Swan, Thomas Edison, Sandor Just, and Franjo Hanaman, the incandescent light bulb becomes commercially available and is still one of the dominant products in the lighting market today. The working principle of an incandescent light bulb, identical to light generated by combustion, is based on blackbody radiation, which states that the emitted electromagnetic spectrum of a blackbody can be related to its temperature. Briefly, the wavelength of emission maximum ($\lambda_{\max}$) can be calculated *via* Wien's displacement law:¹

$$\lambda_{\max} = b/T \quad (\text{Eq 1.1})$$

where T is the temperature of the blackbody and b is a constant with an approximate value of $2898 \mu\text{m}\cdot\text{K}$. To achieve warm white light with the $\lambda_{\max}$ of 580 nm, the required temperature is about 5000 K. However, such an approach is not energy-efficient, and the emitted visible light only occupies a small portion of the spectrum (power efficiency less than 5%) where the other parts are released as heat loss.

At about the same time around the invention of the incandescent light bulb, fluorescent lamp was invented by Peter Copper Hewitt and Edmund Germer, and was finally commercialized by General Electric Co., Ltd. Different from blackbody radiation, fluorescent lamp makes use of photoluminescence, where the emitted ultraviolet light inside the lamp can be directly converted to visible light *via* the inner phosphor coating of the lamp. The power conversion efficiency of this device is about 25%, far higher than that of the incandescent lamp.

Despite the large improvement in power efficiency, fluorescent lamp suffers various issues, such as hazardous materials (e.g., mercury), emitted detrimental ultraviolet (UV) light, and high cost of recycling. Energy-saving and less harmful lighting technology is still demanded for both industrial and residential applications.

Mid-20th century represents the golden age of semiconductor science and technology, and various epoch-making electronic devices were consecutively

invented, namely, p - n junction, bipolar junction transistors, and field-effect transistors.² The birth of p - n junction directly led to the formation of two categories of fundamental optoelectronic devices, photovoltaic cells and light-emitting diodes (LEDs). In 1951, Kurt Lehovec firstly explained the electroluminescence phenomenon in silicon carbide crystals,³ while Richard Haynes and William examined this principle in a standard p - n junction structure made of silicon in 1956.⁴ In this p - n junction, electrons from the conduction band and holes from the valence band will have radiative recombination under electric bias and photons with energy equal to the bandgap of silicon will be released. Such a simple yet elegant working principle gives this new device a relatively high power efficiency.⁵ LEDs were also recognized as a great invention “enabling bright and energy-saving light sources” by the 2014 Nobel Prize in Physics with three awardees working in blue LED developments, namely, Shuji Nakamura, Isamu Akasaki, and Hiroshi Amano.⁶

Besides lighting, another important application of LEDs is the display device. The display is now filled almost in every aspect of our daily life, such as television, cell phone, laptop, and most consumer electronic products. It was even reported that adults in the US spend over 11 hours per day in front of different kinds of “screens”.⁷ The first generation of display is the cathode-ray tube, with ultra-huge size to accommodate the electron gun. In this device, the emitted electron hits the pixels on a phosphorescent screen to produce monochromatic colours. Despite its bulky size, high power consumption, and low efficiency, such a device is still using in some specific areas like graphic design owing to its potentials in pixel colours, response time, and resolution. Currently, the prevailing display types are liquid crystal display (LCD) and organic LED (OLED) display.

In a standard LCD display, a liquid crystal layer is sandwiched between two electrodes as a switch to control the optical transmittance of the polarized backlight *via* red, green, and blue (RGB) filter pixels for colour generation. The backlight is provided normally by a LED device and the core materials are inorganic semiconductors possessing well-defined crystalline structures, such as GaAs (infrared and red), GaP (green), SiC (yellow), and GaN (blue).⁸ LCD device consists of tens of layers, requires complex fabrication techniques (**Figure 1.1**), and suffers issues like limited colour gamut and blue-light hazard. In addition, development in modern technology places increasing demands on both the size and the flexibility (or even the stretchability) on the display. The complex fabrication process flow as well as the rigid material properties severely hinder the application of LCD in large-scale and flexible displays.⁵

Figure 1.1 | The development of display devices. CRT, LCD, and OLED displays are shown by time-market curves. Inset: device structure comparison between OLED and LCD. The figure is modified based on that in literature.^{9,10}

The emerging of OLED display enables the possibility of large-scale displays. Compared with LCD, OLED exhibits various advantages, such as high luminescence (brightness), wide colour gamut, short response time, and low power consumption.¹¹ As shown in the inset of **Figure 1.1**, OLED is much thinner and light is generated by electroluminescence instead of photoluminescence. Despite huge improvements made in OLED display, there is still a large room for further development. For example, the emission intensity and turn-on voltages for different colour pixels in OLED are different, which brings challenges for the circuit design. Furthermore, increasing the applied current density could lead to severe roll-off of device efficiencies in OLEDs. One simple but effective approach to solve this issue is by varying the pixel size for different colours, e.g., large blue pixels and small green or red pixels.¹² However, in practical design, thin-film transistors (TFT), main components in the display for OLED device control (as switches), should also be taken into account, which occupy a certain portion of display surface areas. Therefore, it is impossible to arbitrarily maximize the area size of low-intensity colour pixels and this approach could only improve the display performance marginally.

Exploring new emissive materials provides new possibilities to solve the above issues of OLED.¹³ The materials should possess high electroluminescence, high charge mobility (for low operation voltage), and tunable emission wavelength, compared to organics in OLEDs. In addition, similar to the organics, the materials should also be suitable for low-temperature- and

solution- processing for large-scale display fabrication. The discovery of hybrid organic-inorganic perovskite materials for optoelectronics¹⁴ in 2009 provided a promising candidate although the materials were first used in the photovoltaic cells. These amazing materials possess lots of outstanding optical and electrical properties and are considered as one of the most promising candidates for next-generation lighting and display applications.¹³

Via simple modulation of the composition, dimensionality, and size (in the form of nanocrystals), the emission wavelength (or band gap) can be altered in a wide spectral range from 400 nm to 900 nm, extending to near-infrared (NIR) region, which is highly challenging for organic semiconductor based emissive materials.¹⁵ In this thesis, we will systematically investigate the metal halide perovskite materials as the emissive layer for NIR LEDs and discuss the potential approaches to improve the performance (both the efficiency and the operational stability) of devices with interface-assisted modulation methods.

1.2 Aims and structure of this thesis

Since the first room-temperature operating perovskite LEDs (PeLEDs) were invented in 2014,¹⁶ various strategies have been explored to optimize perovskite emissive layer and potential device configuration, leading to significant enhancement in this newly emerging area. With remarkable contributions from various research groups,^{17–20} the external quantum efficiencies (EQEs) of infrared, red, and green PeLEDs are now over 20%, approaching their commercial inorganic counterparts. However, the device operational stability of PeLEDs remains poor, severely hindering their practical applications.

Although most of the key findings in PeLEDs were made within only 7 years, extensive investigations on OLEDs and perovskite solar cells offer PeLED studies a lot of useful knowledge, which is helpful in achieving high-performance PeLEDs. At the same time, we also notice that systematic investigations of this young technology are still missing. We take the additives, which are widely used to improve the performance of PeLEDs as, an example; a certain additive works for one type of perovskite materials while it exhibits limited function for the other type. As such, a comprehensive and in-depth understanding of PeLEDs (from different aspects) is highly desired, and such investigations would foster further advancements of the PeLED technology for lighting and display applications.

In this thesis, we concentrate on NIR PeLEDs and aim to develop a thorough understanding of the effective approaches based on interface-assisted modulation of the perovskite emissive layer. In short, we systematically studied the critical roles of precursors, substrates, and additives on the film quality of perovskite. With the in-depth understanding of the perovskite crystallization process, we developed a palette of strategies *via* interface-assisted modulation of the perovskite layers, enabling us to achieve NIR PeLEDs with high EQE (23.8 %) and long operational lifetime (T_{70} of 290 hours, the time for the devices to degrade to 70 % of its initial efficiency), representing the state-of-the-art devices.

To present all these results and background knowledge more conveniently, below we present the structure of this thesis as detailed (**Figure 1.2**).

Figure 1.2 | The structure of this thesis.

The fundamental knowledge of perovskite materials will be provided in **Chapter 2**. A brief history, the key physical properties, and crystalline structures of perovskite will be included. In **Chapter 3**, the device structures, working principles, device characteristics, the factors affecting external quantum efficiency (EQE), and the operational stability of PeLEDs will be concisely reviewed. The two chapters form the basis of this thesis.

Chapter 4 will focus on the possible strategies in modulating perovskite emissive layer to achieve high-performance PeLEDs, mainly through composition, additive, and interface engineering. In addition, and the critical

roles of the ZnO interfacial layer in modulating perovskite film (e.g., molecular reactions and crystallization) and PeLEDs will be systematically discussed.

Chapter 5 is dedicated to the experimental and characterization techniques that are relevant to the studies in the thesis. We will pay attention to the basic principles of the methods and how they were utilized in our studies.

Chapter 6 will be a summary of the key results of the appended papers. We will also make a brief discussion on the prospects of PeLED research, including the challenges and opportunities. This amazing technology is promising to be the dominant products in the lighting and display markets in the near future.

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2

Metal Halide Perovskite

Metal halide perovskite is a class of crystalline materials with the general formula of ABX_3 and is the core material used in this thesis. In this chapter, we will briefly review its history, crystalline structures, and intriguing physical properties.

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2.1 The emergence of metal halide perovskite

The word "perovskite" is created in memory of Russian mineralogist Lev Perovski, who first discovered this new category of minerals in the Ural Mountains.¹ Although the first type of perovskite is calcium titanate ($CaTiO_3$), nowadays any materials adopting the general formula ABX_3 could be referred to as perovskites (**Figure 2.1**). In this thesis, we will focus on metal halide

perovskite (MHP), wherein the formula, A is typically a monovalent cation, B is a divalent metal cation (e.g., Pb^{2+} or Sn^{2+}), and X is a halide anion (e.g., Cl^- , Br^- or I^-). In the crystal structure, X anions bond with B cation to form $[\text{BX}_6]^{4-}$ octahedra (shaded in **Figure 2.1a**), which is the skeleton of perovskite crystals.² The six X anions of the octahedra are located at the face centres of the simple cubic crystal made of A cations. The commonly used A cations can be either inorganic (e.g., Cs^+) or organic [e.g., methylammonium (MA^+) or formamidinium (FA^+), see **Figure 2.1b**]. Those with organic cations are also referred to as hybrid organic-inorganic perovskites.

Figure 2.1 | Crystallography of perovskite. a, Crystal structure of perovskite materials. b, Methylammonium (MA^+) and formamidinium (FA^+) cations.

Despite the first report in 1884,³ the application of perovskites in optoelectronics was not explored until 1990s, pioneered D. Mitzi.⁴ The perovskites used in those studies possess long organic A cations; these perovskites are referred to as two-dimensional Ruddlesden-Popper perovskites.⁵ More recently in the past decade, benefiting from the rich experience from other solution-processed optoelectronic devices (including organic optoelectronics and also dye-sensitized solar cells), the development of MHP for optoelectric devices has developed very quickly. These development started with the pioneering work Tsutomu Miyasaka, who employed self-assembled organic-inorganic perovskite to replace organic dyes on TiO_2 in dye-sensitized solar cells with an efficiency of 3.8 %.⁶ The efficiency was rapidly refreshed to about 9.7 % with the introduction of spiro-MeOTAD as the solid hole conductor⁷ and then to 11 % with alumina replacing TiO_2 as an inert scaffold in the device structure.⁸ The community started to realize that perovskite can convert photons to free electrons and holes.⁹ From

then, the planar heterojunction structure, which is widely used in organic electronic devices, was widely accepted and became a popular device configuration for perovskite solar cells.

Photovoltaic technology based on perovskite materials is regarded as one of the huge scientific breakthroughs in the past years and was selected as the “top 10 of the year” by *Science* journal in 2013.^{10,11} It is widely known in the semiconductor community that a good material for solar cells also shows excellent properties for LEDs. Compared with conventional inorganic semiconductors like Si or GaAs, perovskite presents a large absorption coefficient, high photoluminescence, and high defect tolerance.¹² Compared with their organic counterparts, perovskite shows excellent charge transport properties (e.g., high mobility) and high colour purity (narrow emission peak width). Specifically, by tuning the composition, dimensionality of perovskites and the size of the perovskite nanocrystals, the bandgap (emission peak wavelength) can be precisely tuned in a relatively wide spectral range from ultraviolet to near-infrared (NIR).¹³ All these properties make perovskite promising for LEDs.

Figure 2.2 | The device efficiency chart of PeLEDs in different colours. In the figure, EQE stands for external quantum efficiency, an important parameter for LEDs (see Chapter 3).

The first attempt to fabricate LEDs using perovskite materials was made in 1994, but the device could only operate at liquid nitrogen temperature.¹⁴ In 2014, a team at Cambridge University led by Prof. Richard Friend reported room-temperature PeLEDs for the first time, with the device efficiencies about 1 % for NIR and around 0.1 % for green colour.¹⁵ Currently, the efficiencies for red, green, and NIR are all above 20 %, while the efficiency of blue LEDs is

over 12%.¹⁶ **Figure 2.2** summarizes the progress of PeLEDs in recent years. Currently, the PeLED efficiencies of most colours already meet the requirements of practical products, and one of the most challenging barriers for PeLED commercialization would be the device operational stability.

The great achievements of perovskites in optoelectronic devices can be attributed to both their physical properties (will be discussed in the next section) and crystal structures. Generally, MHP has three typical crystal structures: cubic, tetragonal, and orthorhombic. The transitions between these structures are reversible and can be triggered by changes in temperature or exchanges of halogen ions. The cubic structure possesses a higher degree of symmetry and is usually more thermodynamically stable compared with the tetragonal and orthogonal counterparts. There are various criteria to determine whether the cubic phase perovskite crystal is theoretically stable, and the commonly used ones are Goldschmidt tolerance factor (t_f) and octahedral factor (μ). The definitions of the two factors can be illustrated by¹⁷

$$t_f = (R_A + R_X) / \sqrt{2}(R_B + R_X) \quad (\text{Eq 2.1})$$

$$\mu = R_B / R_X \quad (\text{Eq 2.2})$$

where R_A , R_B , and R_X are the effective ionic radii of A, B, and X ions, respectively. Goldschmidt tolerance factor is an indicator of the state of disorder in the system while octahedral factor describes the stability of $[\text{BX}_6]^{4-}$ octahedra in the perovskite crystal.¹⁷ For MHP to form stable crystal structures, t_f and μ should be in a range from 0.81 to 1.11, and 0.44 to 0.90, respectively.¹ It tends to form a cubic phase if t_f lies in $0.89 \leq t_f \leq 1$. However, if t_f falls in other ranges, the formed crystals could be either tetragonal or orthorhombic phase. Therefore, it is important to precisely control the radii of all constituent ions to form stable cubic perovskite phases for high-performance devices.¹⁸ Typical ions used in MHP and their effective radii are listed in **Table 2.1**.

The structural distortion of crystals can have an impact on the properties of perovskite and partial or complete substitution of cations or anions can significantly modulate the physical properties of the perovskite.¹⁹ For instance, both MAPbCl_3 and MAPbBr_3 present cubic structure, however, MAPbI_3 exhibits unstable tetragonal phase at room temperature due to the size difference of X anions (**Table 2.1**). The obvious degradation of the solar cells based on MAPbI_3 upon exposure to the atmosphere with relative humidity (RH) $\geq 55\%$ is due to this unstable tetragonal structure.²⁰ To eliminate this poor stability issue, introducing a certain amount of bromine during the preparation

can help to convert it into MAPb(Br_xI_{1-x})₃ ($x \geq 0.2$) with a stable cubic structure. As demonstrated by Noh *et al.*, such an approach can significantly improve the device lifetime in humidity.²⁰

Table 2.1 | The effective radii for typical ions in halide perovskites.

	Ions	Effective radii
A ⁺	FA ⁺	2.53 Å
	MA ⁺	1.80 Å
	Cs ⁺	1.67 Å
B ²⁺	Pb ²⁺	1.19 Å
	Sn ²⁺	1.18 Å
X ⁻	Cl ⁻	1.81 Å
	Br ⁻	1.96 Å
	I ⁻	2.20 Å

2.2 The optoelectronic properties of perovskite

The great success of perovskite as optoelectronic material is related to its excellent optical and electronic properties. All these result from the band structure of perovskites, on which we will make a brief review in this section.

2.2.1 Band structure and tunable bandgap

Most of the metal halide perovskites widely explored for optoelectronic devices are direct bandgap semiconductors, where their conduction band minimum (CBM) and valence band maximum (VBM) are located at the same momentum in the *E-K* diagram. The difference between CBM and VBM thus defines the bandgap of the perovskites.

Herein, we use formamidinium lead triiodide (FAPbI₃) to schematically show the simplified band structure of perovskite materials (**Figure 2.3**).

As illustrated in **Figure 2.3a**, the band edges of MHPs are defined by the antibonding atomic orbitals of [PbI₆]⁴⁻ octahedra. The CBM is created by the antibonding hybridization of Pb (6p) orbital and I (5s) orbital, with the main contribution from the former one. The antibonding hybridization of Pb (6s) orbital and I (5p) orbital gives rise to the VBM, where the latter plays a more important role.²² Although A cation (in this case, FA) does not directly influence

the formation of CBM or VBM, it can still alter the bandgap or photoluminescence of the perovskite. For example, A cations can affect the covalent and ionic bonding between B cations and X anions, and therefore alter the band gap and photoluminescence of perovskites.²³ In **Paper 2** appended in this thesis, we introduced ion exchange between FA and Cs cations with the assistance of interface, and successfully achieved tunable electroluminescence ranging from 715 nm to 800 nm.

Figure 2.3 | Schematics of band diagram of FAPbI₃. **a**, The simplified band structure of FAPbI₃. **b**, Defect tolerance of semiconductor materials (top one: defect-intolerant, bottom one: defect-tolerant).

Choosing certain halogen ions or alloying the halogen elements in different ratios can efficiently modulate the band gap of MHP, tuning the emission peak wavelength (or colour) from violet to near infrared (NIR), as presented in **Figure 2.4**. The tunable bandgap forms a unique property of perovskites, although it may cause the spectral instability owing to the phase segregation in mixed halide perovskites.

In addition to the composition, the modulation of dimensionality or the size of perovskite quantum dots can also result in a large variation of the band gap, due to quantum confinement effects. For instance, with the introduction of long-chain organic molecules [e.g., C₄H₉NH₃I (BAI) and C₈H₉NH₃ (PEA)] in the perovskite precursor solution, these molecules can act as spacer layers between the [BX₆]⁴⁻ octahedrons and prevent the formation of three-

dimensional crystal structures of perovskite.^{24,25} The obtained perovskites are mostly defined as quasi-two-dimensional (quasi-2D) or two-dimensional (2D) perovskites. Such methods for dimensionality reduction lead to an increase in the band gap and a decrease in the electrical properties. For perovskite quantum dots, the particle size control during the synthesis also shows a large effect on the band gap modulation.

Figure 2.4 | Schematic illustration of tunable emission of perovskites. By altering the halogen element (or alloying), we can shift the photoluminescence in a wide spectral range from violet to near infrared.

2.2.2 Defect and defect tolerance

For crystalline materials, defects typically generate in the crystal growth process, including point defects (like atom vacancies, interstitials, and anti-site substitutions), dislocations, grain boundaries, precipitates and impurities.²⁶

Different from conventional inorganic semiconductors, perovskite films are mostly processed from solution and therefore contain lots of defects, which are usually detrimental for perovskite optoelectronic devices. Most of the defects originate from the non-stoichiometric compositions at crystal surfaces and the sublimation or decomposition of organic molecules (e.g., FA and MA) during thermal annealing in the film deposition process. It is widely accepted that most of the defects exist at the grain boundaries and crystal surfaces for perovskite thin films.²⁷ The defects in perovskites can be divided into either deep defects or shallow defects. Deep defects have a larger impact on the optoelectronic properties of the materials. And shallow defects can also significantly affect the device performance.^{28,29}

Most of point defects are shallow states and locate within the valence or conduction band, or near the band edge in perovskite. These defects have limited effects on the emission properties of perovskite. Therefore, perovskite can still exhibit high PL emission even with a high defect density (e.g., 10^{13} - 10^{15} cm⁻³).³⁰ This is a distinctive characteristic of perovskite compared with other conventional semiconductors (such as GaAs or CdSe), where most of defects are mid-gap states with higher formation energy. These defects can act as non-radiative recombination centres, resulting in reduced photoluminescence or electroluminescence of perovskites. Therefore, we can regard the perovskite as a “defect-tolerant” semiconductor, while the conventional inorganic semiconductors (e.g., GaAs) as “defect-intolerant” materials (**Figure 2.3b**).

2.2.3 Narrow emission bandwidth

As shown schematically in **Figure 2.4**, the emission spectra of perovskites exhibits a narrow bandwidth. The full width at half maximum (FWHM) of its electroluminescence and photoluminescence spectra are normally less than 100 meV.^{31,32} Such narrow emission bandwidth leads to high colour purity of perovskites, which is highly favourable for LED lighting and display.

The origins for narrow emission bandwidth could be traced back to the crystal structures of perovskites, where the Fröhlich interaction between carriers and longitudinal optical phonons exists and mainly contribute to the homogeneous linewidth broadening of three-dimensional structure of perovskites.³³ In addition to this, (**Section 2.2.2**), shallow or intra-band defects can be passivated efficiently, while mid-gap defect states in perovskites mostly act as non-radiative recombination centres, contributing negligibly to the broadening of the emission bandwidth.²¹

2.2.4 Charge carrier dynamics

The absorption of a photon or electric injection of holes and electrons in semiconductors generates an exciton, an electron-hole pair with certain binding energy. For three-dimensional perovskite, the binding energy is about 2 to 60 meV, approximately the thermal energy provided by room temperature (25 meV).^{2,34} Hence, the injected carriers in perovskite tend to present as free charge carriers, instead of tightly bound excitons in organic emissive materials. The recombination of these carriers could create light emission and therefore, the recombination pathways define the optoelectronic properties of the

semiconductors. There are three general recombination mechanisms in semiconductors, *i.e.*, Shockley-Read-Hall (or trap-assisted), radiative, and Auger types (**Figure 2.5**).

Shockley-Read-Hall recombination is mostly related to the defect states of the perovskite, including lattice defects and dangling bonds at grain boundaries that can trap the free carriers (**Figure 2.5**). And the rate of this recombination is proportional to the density of defect states and free carriers. Auger recombination (**Figure 2.5**) usually occurs under high carrier densities. This process involves three particles: the energy released by the recombination of a pair of free carriers is transferred to a third carrier. Thus, its recombination rate is proportional to the cube of free carrier density. Both mechanisms are non-radiative recombination, which could hardly provide light emission and should be avoided in high-efficiency LEDs.

Figure 2.5 | Schematics of recombination mechanisms in a semiconductor.

Radiative recombination (**Figure 2.5**) in a band-to-band way, creates light emission (*via* either photoluminescence or electroluminescence). The radiative recombination rate is hence proportional to the square of free carrier density. With all above, we are able to describe the carrier dynamics of the perovskite systems using the continuity equation:

$$\frac{dn}{dt} = G - R \quad (\text{Eq 2.3})$$

where n is the free carrier density, t is the time, G is the generation rate of free carriers, and R is the overall recombination rate of free carriers and can be calculated by:

$$R = k_1 n + k_2 n^2 + k_3 n^3 \quad (\text{Eq 2.4})$$

where k_1 , k_2 , and k_3 are the recombination coefficients for Shockley-Read Hall (or monomolecular), radiative (or bimolecular), and Auger recombination types. Previous investigation indicates that the order of magnitude of k_1 , k_2 , and k_3 of MHP are 10^6 s^{-1} , $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $10^{-28} \text{ cm}^6 \text{ s}^{-1}$, respectively. The relatively large k_1 indicates a high density of defects. Therefore, it is necessary to utilize defect passivation methods to reduce defect density, in order to increase the percentage of radiative recombination at low injected free carrier density.¹⁹

Based on **Eq 2.3** and **Eq 2.4**, we can determine which type is dominant in the perovskite in different situations (free charge carrier density). For example, when the injected free carrier density is low ($10^{13} - 10^{15} \text{ cm}^{-3}$), the Shockley-Read-Hall (or trap-assisted) is the primary recombination type, while Auger plays the main role for perovskite with a high injected free carrier density ($> 10^{18} \text{ cm}^{-3}$).³⁰ The intermediate carrier density ($10^{16} - 10^{18} \text{ cm}^{-3}$) is preferred for LEDs since the increased free carriers can fill the defects in the perovskite and effectively enhance the percentage of radiative recombination. Furthermore, such carrier concentration can improve the overlapping of the wavefunctions of holes and electrons, increasing the chance for their recombination.^{19,30}

In addition to these, unbalanced injection of electrons and holes, or poor carrier transport in the emissive layer, resulting in carriers accumulating at the interface, can also lead to non-radiative recombination. All these have to be taken into consideration during the device structure design.

2.2.5 Photoluminescence quantum efficiency

Photoluminescence generate free carriers into the semiconductor by light, with certain photon energy (above the band gap of the semiconductor). The photoluminescence quantum efficiency (PLQE) provides a quantitative way to determine the external efficiency of photoluminescence, and can be calculated by:

$$PLQE = \frac{\text{number of emitted photons}}{\text{number of absorbed photons}} \quad (\text{Eq 2.5})$$

For perovskites, the situation could be complicated, due to the optical interference effect and potential photon recycling effect (the re-absorption of emitted photons). Therefore, PLQE is one of the critical criteria to evaluate the efficiency of radiative recombination (emission) in perovskites.^{30,35}

Using **Eq 2.5**, we can derive the analytical formula for PLQE for three-dimensional perovskite:

$$PLQE = \frac{k_2 n}{k_1 + k_2 n + k_3 n^2} \times 100 \% \quad (\text{Eq 2.6})$$

Obviously, PLQE has a strong dependence on the free carrier density, which can simply be modulated by the laser intensity.³⁰ Thus, with the curve of PLQE *versus* laser intensity, we can easily filter out the limiting bottleneck of efficient photoluminescence and more details on this will be introduced later in **Section 5.3**.

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Perovskite Light-Emitting Diodes

In this chapter, we will pay attention to the basic information of LEDs, including working principles, device characteristics, and their characterization techniques. In the last two sections, we will briefly discuss the key factors affecting the device efficiency and stability.

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3.1 Working principles

Light-emitting diodes (LEDs) are solid-state optoelectronic devices utilizing injected electricity (electrons and holes) to generate light. While conventional inorganic LEDs make use of the p-n junction for charge injection and

recombination, perovskite LEDs (PeLEDs) rely on the charge-transport layers for charge injection and the perovskite layer for radiative recombination. More specifically, a typical PeLED (**Figure 3.1**) consists of multiple layers with different functions: transparent electrodes, opaque metal electrodes, hole transport layers (HTLs), electron transport layers (ETLs), and emissive layers made of perovskites with thicknesses usually in the scale of tens of nanometers. The stacking order of the layers can follow either conventional or inverted configuration (see **Figure 3.1a**) depending on specific needs.

Figure 3.1 | Schematics of PeLED device configurations. **a**, Conventional (or *p-i-n* structure) and inverted configuration (or *n-i-p* structure). **b**, The operation mechanism of a PeLED.

In the device, the commonly used transparent electrode is indium-tin-oxide (ITO)-coated glass, while the opaque metal electrodes (e.g., Ag, Au, or Al) are usually deposited by thermal evaporation. Based on the device configurations, the transparent electrode acts as either the cathode or the anode of the PeLEDs.

The operation mechanism of the PeLEDs is schematically shown in **Figure 3.1b**.¹ Firstly, the application of a bias on both electrodes can inject electrons and holes into the emissive layer *via* ETL and HTL, respectively. Secondly, electrons and holes meet each other inside the emissive layer and undergo radiative recombination to form photons or non-radiative recombination to release the energy in other forms (e.g., heat loss). Lastly, the generated photons need to escape from the device (e.g., by refraction) and emit light.

A combination of the above mentioned four processes (*i.e.*, injection, transport, recombination, and light extraction) determines the final efficiency of the device, while the emission peak wavelength of PeLED is mainly determined by the bandgap of the employed perovskite emissive layer. To achieve high efficiency, a PeLED needs to meet several requirements, including but not limited to, (i) balanced injection and transport efficiencies for both electron and

hole; (ii) suitable energy level alignment for different layers; and (iii) high PLQE perovskite layer (radiative recombination is the dominant pathway for carriers). Detailed discussion on the device efficiency can be found in **Section 3.3**.

3.2 The characteristics of LEDs

The device performance of LEDs can be systematically evaluated by a set of key parameters, such as luminance/radiance, peak wavelength, device efficiency, and operational stability. The measurement or calculation of all these parameters can be obtained *via* electrical and spectral measurements. In this section, we will briefly introduce some of these parameters, based on the testing platform in our lab.

3.2.1 Key parameters

The spectral radiant flux ($\Phi_{e,\lambda}$) is the emitted radiant energy per unit time at a certain wavelength. The integration of the spectral radiant flux over the whole spectral range gives the radiant flux (Φ_e) of the material:¹

$$\Phi_e = \int \Phi_{e,\lambda} d\lambda \quad (\text{Eq 3.1})$$

where λ is the wavelength. Such radiometric quantity is normally utilized for near-infrared (NIR) light, while for the visible light, we prefer to use its photometric counterpart, luminous flux:¹

$$\Phi_v = K_m \int \Phi_{e,\lambda} \bar{y}(\lambda) d\lambda \quad (\text{Eq 3.2})$$

where K_m is a scaling factor (luminous efficacy, 683.002 lm/W) and $\bar{y}(\lambda)$ is the luminosity function describing the average spectral sensitivity of human eyes regarding the brightness of different colors (wavelengths). Varying the illumination condition could change the luminosity function and for photopic case (10 to 10^8 cd/m²), the peak position of this function is about 555 nm (**Figure 3.2a**).¹

Since the radiant flux has a spatial distribution, a more convenient way to describe the quantity would be radiance L_e , which is defined as:¹

$$L_e = \frac{\partial^2 \Phi_e}{\partial \Omega \partial S \cos \theta} \quad (\text{Eq 3.3})$$

where S is the emitting area of the light source, θ is the azimuthal angle of the detector position, and Ω is the solid angle (**Figure 3.2b**), which can be calculated by:¹

$$d\Omega = \frac{dA}{R^2} = \frac{Rd\theta \cdot R\sin\theta d\varphi}{R^2} = \sin\theta d\theta d\varphi \quad (\text{Eq 3.4})$$

where A is the area size of the detector, and R is the distance between the light source and the detector. The use of radiance can eliminate the unclear description of radiant flux variation in the space due to detecting angle and distance. Similarly, the luminance is defined as:¹

$$L_v = \frac{\partial^2 \Phi_v}{\partial \Omega \partial S \cos\theta} \quad (\text{Eq 3.5})$$

Figure 3.2 | Schematics of luminosity function (a) and radiance (b) for LEDs.

Most of PeLEDs could be considered as Lambertian scatterers, where the radiance I_e or luminance intensity I_v (radiant or luminous flux at a certain solid angle) follows a cosine law:^{1,2}

$$I_e(\theta) = I_{e0} \cos\theta \quad (\text{Eq 3.6})$$

where I_{e0} is the radiant intensity at azimuthal angle of 0° . Using **Eq 3.6**, we can find that the radiance of a Lambert radiator at different azimuthal angles is a constant:

$$L_e(\theta) = \frac{I_e}{dS \cos\theta} = \frac{I_{e0}}{dS} = \text{constant} \quad (\text{Eq 3.7})$$

Combining **Eq 3.3**, **3.4** and **3.7**, we have a new formula for radiant flux:

$$\Phi_e = \int_0^{2\pi} \int_0^{\pi/2} \int_0^S L_e \cos\theta \sin\theta \, dS \, d\theta \, d\varphi = \pi S L_e \quad (\text{Eq 3.8})$$

or luminous flux:

$$\Phi_v = \pi S L_v \quad (\text{Eq 3.9})$$

With these, we are able to use the measured radiance to calculate the radiant flux, and further to different efficiencies. The power efficiency of the device, η_{power} , is defined as the conversion efficiency between input electric power and output optical power (luminous flux):¹

$$\eta_{power} = \frac{\Phi_v}{J \cdot S \cdot V} = \frac{\pi L_v}{J \cdot V} \quad (\text{Eq 3.10})$$

where J and V are the measured electric current density and the applied bias of the device, respectively. The wall-plug efficiency, η_{wpe} , is equivalent to the power efficiency, using radiant flux as the numerator:¹

$$\eta_{wpe} = \frac{\Phi_e}{J \cdot S \cdot V} = \frac{\pi L_e}{J \cdot V} \quad (\text{Eq 3.11})$$

Current efficiency, η_{cu} , is defined as the ratio of luminance to current density:¹

$$\eta_{cu} = \frac{L_e}{J} = \frac{\Phi_e}{J \cdot S \cdot \pi} \quad (\text{Eq 3.12})$$

The ratio of the number of emitted photons (n_p) to the number of ejected charge carriers (n_e) gives the external quantum efficiency (EQE), η_{ext} :¹

$$\eta_{ext} = \frac{n_p}{n_e} = \frac{t \cdot \int \Phi_{e,\lambda} \cdot (\lambda/hc) \cdot d\lambda}{\int J \cdot S/e \cdot dt} \quad (\text{Eq 3.13})$$

where h is the Planck constant, c is the speed of light, e is the elemental charge, and t is the time span for the measurement. There are various factors affecting the EQE of PeLEDs which will be thoroughly discussed in **Section 3.3**.

Figure 3.3a shows a typical current density-voltage-radiance (J - V - R) curve of a NIR LED. **Figure 3.3b** shows an illustration of the EL spectrum of a typical NIR LED, where we can identify the peak wavelength (λ_{max}) and emission bandwidth (full width at half maximum, $FWHM$) of the emission. We note that the commonly used Commission Internationale de l'Eclairage (CIE) coordinates to quantitatively characterize the visible colour⁴ are not suitable for our NIR LEDs, and we still keep using the λ_{max} and the $FWHM$ to evaluate the emission spectra for our devices.

Operational stability which is typically described by the operating time needed for the luminance or radiance to drop to a specific ratio of their initial value (for examples, 50%, that is T_{50} ; 70%, that is T_{70}), is another key parameter of LEDs

for their practical applications. A summary of commonly used key parameters of LED are listed in **Table 3.1**.

Figure 3.3 | Schematic illustration of current density-voltage-radiance (a) and EL (b) curves for a NIR LED.

Table 3.1 Key parameter list of LEDs.

Parameters	Symbols	Units	Definitions or notes
Radiance	L_e	$W \cdot sr^{-1} \cdot m^{-2}$	Power per area per solid angle
Radiant intensity	I_e	$W \cdot sr^{-1}$	Power per solid angle
Radiant flux	Φ_e	W	Energy per unit time
Luminance	L_v	$cd \cdot m^{-2}$	Power per area per solid angle
Luminous intensity	I_v	$cd (lm \cdot sr^{-1})$	Power per solid angle
Luminous flux	Φ_v	lm	Energy per unit time
Peak wavelength	λ_{max}	nm	Wavelength of highest emission
Peak broadening	$FWHM$	$nm (eV)$	Full width at half maximum
Chromaticity	(x, y)	-	Coordinates in CIE 1931 space
Current density	J	$mA \cdot cm^{-2}$	Current density at the forward bias
EQE	η_{ext}	%	External quantum efficiency
Power efficiency	η_{power}	$lm \cdot W^{-1}$	Optical/electric power conversion efficiency
Wall-plug efficiency	η_{wpe}	%	Optical/electric power efficiency
Current efficiency	η_{cu}	$cd \cdot A^{-1}$	Luminous/current density ratio
Operational lifetime	T	h	Operating time for luminance or radiance to degrade to a certain level of their initial value

3.2.2 LED characterization platform

In our lab, we characterize the as-fabricated PeLEDs using a home-built testing platform within a nitrogen-filled glove box at room temperature. A schematic illustration of this setup is displayed in **Figure 3.4** and will be briefly described as below.

The testing platform consists of four main parts, including a source meter, a spectrometer, an integrating sphere, and a microcontroller (computer) for measurement control and data recording. We use a KEITHLEY 2400 as the source meter, which performs voltage bias sweeping on the LEDs and collects the corresponding electrical current. The emitted light from the device is characterized by the spectrometer (QE Pro, Ocean Optics). The LED device is placed on the top of the integrating sphere with its transparent electrode side towards the input port of the sphere. The active area of the LED (overlapping part of transparent and opaque electrodes) should be positioned in the center of the input port. The integrating sphere and the spectrometer are connected *via* a 1000 μm optical fiber. A custom-made LabVIEW program in the computer is used to collect measurement data and generate current density-voltage-radiance (J - V - R) curves, EQE-voltage/current density curves, EL curves and CIE coordinates of the LED.

Figure 3.4 | Schematic illustration of the home-built LED test platform.

To ensure accurate measurements of our devices, we need to calibrate the testing platform with a Visible-NIR radiometric calibration source (for absolute light intensity accuracy) and an HG-1 light source (for wavelength accuracy). This provides us with a calibration curve, C_{λ} , which is used to translate the photon counts at different wavelengths (energies) into radiance. During the measurement, both EL spectra of the LEDs without and with bias will be

collected as D_λ and S_λ , respectively. With an integrating time of t , we can therefore obtain the spectral radiant flux:

$$\Phi_{e,\lambda} = \frac{(S_\lambda - D_\lambda) \cdot C_\lambda}{\Delta\lambda \cdot t} \quad (\text{Eq 3.14})$$

With this and J - V - R curves, we can obtain almost all key parameters of LED listed in **Table 3.1** through **Eq 3.1** to **Eq 3.13**.

3.3 External quantum efficiency

According to the definition of EQE and the working principles of a LED in previous sections, we can further elaborate on the determining factors of EQE from the perspective of the four processes in LED operation.

We define the internal quantum efficiency (IQE, η_{int}) as the conversion rate of injected carriers into photons and the out-coupling efficiency (η_{oc}) or light extraction efficiency as the portion of generated photons that can be emitted. Hence, we can express the EQE of the device as:^{1,2}

$$\eta_{ext} = \eta_{int} \cdot \eta_{oc} \quad (\text{Eq 3.15})$$

The IQE can further be described as:^{1,2}

$$\eta_{int} = \eta_{inj} \cdot \eta_{rad} \quad (\text{Eq 3.16})$$

where η_{inj} is the carrier injection efficiency (relating to the electron-hole injection and transport balance) and η_{rad} is the radiative recombination efficiency. For PeLEDs with 3D perovskites, the radiative recombination efficiency can be approximated as the PLQE (see **Section 2.2.5**).

Eq 3.15 and **Eq 3.16** provide us the fundamental strategies to enhance the EQE of a LED, *i.e.*, improving the electron-hole injection balance, radiative recombination, and light out-coupling.

3.3.1 Internal quantum efficiency

Electron-hole balance and radiative recombination are two key factors for IQE (see **Eq 3.16**). The balance between electron and hole includes both the charge carrier injection and transport within the LED and many critical factors can play important roles, including charge carrier mobility, energy level alignment, and defect states of the charge injection layers. Unbalanced injection and transport lead to the accumulation of carriers within one side of

the device, resulting in Auger recombination and low radiative recombination efficiency.

The charge carrier velocity (v) within a layer is determined by its mobility (μ):⁵

$$v = \mu E = \mu V/d \quad (\text{Eq 3.17})$$

where E is the electric field intensity, V is the applied bias, and d is the thickness of the layer. Thus, the carrier mobilities of the hole and electron injection layers are expected to be comparable in PeLEDs.⁵

Figure 3.5 | Schematic illustration of energy level alignment of different ETL, HTL, and perovskite materials. PVK: poly(9-vinylcarbazole); TPBI: 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole); PCBM: phenyl-C₆₁-butyric acid methyl ester; F8: poly(9,9' -dioctylfluorene); PEI: polyethyleneimine; BPC: 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; TFB: poly((9,9-dioctylfluorenyl-2, 7-diyl)-co-(4,4'-(N-(4-secbutylphenyl)diphenylamine); PEDOT-PSS: Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate); DMSO (dimethyl sulfoxide); CBP: 4,4'-Bis(N-carbazolyl)-1,1'-biphenyl; TPD: poly(N,N'-bis (4-butylphenyl)-N,N'-bis(phenyl)benzidine); and SOCP: self-organized conducting polymer blend of PEDOT-PSS, PFI (tetrafluoroethylene-perfluoro-3,6-dioxa-4-methyl-7-octenesulfonic acid copolymer). Energy level values in the figure are collected from literature^{6,7}.

Furthermore, the interfacial energy barriers caused by the energy level alignment form another critical factor influencing the IQE. A good carrier confinement structure formed by using suitable ETL and HTL materials for a certain perovskite material is desirable in improving the radiative recombination efficiency (**Figure 3.5**). In the confinement structure, the electron (hole) injection layer also acts as a hole (electron) blocking layer and thus efficiently confines the charge carriers within the perovskite for radiative recombination. To realize this, the conduction band minimum (valence band

maximum) of the HTL(ETL) layer should be higher than that of the perovskite layer, while the valence band maximum (conduction band minimum) of HTL (ETL) should be deeper than (or comparable to) that of the perovskite layer. **Figure 3.5** lists the energy levels of some commonly used ETL, HTL, and perovskite materials. For NIR PeLEDs presented in this thesis^{3,8}, ZnO/PEIE (polyethyleneimine ethoxylated) and TFB are highly suitable for FAPbI₃.

The defect density of the ETL and HTL also affects the injection efficiency and passivation of these layers is necessary. For example, metal oxides including ZnO, TiO_x, and NiO_x prepared *via* low-temperature solution method, are widely used as the carrier injection (or interfacial) layers of perovskite optoelectronic devices.⁹ The relatively high defect density is an important challenge for their applications in LEDs, in addition to their mismatched energy levels with perovskites. These issues can be solved by inserting modifying materials, such as PEIE, PEI and PCBM,^{3,8,10–12} to passivate the defects, adjust energy levels, improve interface contact, or balance the electron/hole transport.

Radiative recombination efficiency is more related to the thin film quality of the perovskite emissive layers and defect states. More details on this will be discussed in **Chapter 4**, including the defect passivation and the modulation of perovskite film formation.

3.3.2 Light out-coupling

Light out-coupling can be affected by the structure of the LED, and the refractive index and film morphology of each layer in the LED. **Figure 3.6** presents a schematic illustration of some typical loss mechanisms in the LED, which we will briefly introduce in the following text.

When light is propagating from a high refractive index material to a low refractive index material, a critical angle exists defined by Snell's law. Beyond this angle, the emitted light will be completely reflected back to the perovskite layer (total internal reflection). This phenomenon creates the substrate mode and waveguide mode of the LED.

For the emitted light towards the metal (opaque) electrode, it can excite the surface plasmon polaritons (SPPs) at the HTL/metal interface. SPPs can absorb a large portion of the light and further reduce the emitted light. In addition, the perovskite material itself can absorb a part of the light (internal absorption or self-absorption). Considering all the above mechanisms, the

estimated out-coupling efficiency of a PeLED would be less than 25 % without special out-coupling designs.^{13,14}

Figure 3.6 | Schematic illustration of light out-coupling in a perovskite LED. Different loss mechanisms and refractive index of some layers are indicated.

The enhancement of out-coupling efficiency could significantly improve the EQE of PeLEDs and various strategies have been borrowed from the relatively mature OLED and quantum dot LED (QLED) technologies. For instance, the patterned ITO or metal electrode with designed micro-/nanostructures is proved to be useful for PeLEDs.^{15,16} To deal with the self-absorption of perovskites, optimizing the emissive layer thickness and the electrode area is an effective solution. In 2018, Jianpu Wang's group demonstrated that the light out-coupling efficiency of PeLEDs can reach 30 % (with device EQE of 20.7 %) by using isolated perovskite platelets (with the size of micrometers) as the emissive layer.¹⁷ These platelets could randomly scatter light and effectively improve light out-coupling. This method, by modulating the morphology of perovskite structures, is simple and does not require any complicated fabrication techniques. Compared to other strategies based on precise optical design, EL of the PeLEDs in this case exhibits low dependence on either wavelength or viewing angle, which is promising for practical applications.

3.4 Operational stability

The operational stability of PeLEDs remains one of the key challenges for their commercialization. Although the half-lifetime of NIR PeLEDs³ is approaching 700 hours at a current density of $20 \text{ mA} \cdot \text{cm}^{-2}$, the half-lifetime of PeLEDs

emitting visible colours is only 250 hours at a relatively low luminance of 100 $\text{cd}\cdot\text{m}^{-2}$.¹⁸ Especially for blue PeLEDs, the half-lifetime is even worse to be only a few minutes.¹⁹ Up to now, the operational stability of PeLEDs can not compete with that of OLEDs and QLEDs¹⁴. The main limiting factors for this poor stability of PeLEDs include phase instability, ion migration, thermal instability, and interface instability.

The instable phase introduces a detrimental effect on device stability, including phase transition and separation of perovskite. The perovskite with less favorable tolerance factor can undergo phase transition easily upon the change of temperature or moisture (**Section 2.1**). The phase separation commonly occurs in perovskite with mixed halogen elements (e.g., $\text{FAPbI}_{3x}\text{Br}_{3(1-x)}$), where phase-segregated Br-rich and I-rich domains can form under the electric field as a result of ion migration.

Indeed, ion migration is an important issue in PeLED, seriously affecting the device operational stability. It leads to lots of detrimental effects, including but not limited to the formation of new defects, the accumulation of charged ions at the interfaces, and the decomposition of electrodes.¹ The defects, on surfaces and grain boundaries, especially the halide vacancies, could provide sufficient space for ion migration and make the migration paths less blocked. Therefore, defects elimination is one of the most effective methods to prevent ion migration in the perovskite film, and can be achieved by efficient defect passivation and perovskite crystallization modulation. Compared with perovskite photovoltaics, PeLEDs show higher tolerance to additives due to their less strict requirements on carrier mobility. Thus, it is possible to reduce the defect density by exploiting various additives at a large amount.

The thermal stability issue of perovskites is associated with materials decomposition and changes in bandgap (emission peak wavelength) during heating. The phenomenon of bandgap changing is severe in some mixed-dimensional perovskites, which undergo phase transition from wide-bandgap to narrow-bandgap phases upon heating and lead to the red shift of PL and EL. In addition, the required annealing time for some highly emissive perovskite preparation is short at low temperature (e.g., below 100 °C for several minutes). The emission intensity and PLQE of perovskite films might have a significant decrease by further increasing temperature or duration of the annealing process. Hence, perovskites might have permanent damages during device operation, due to the additional “annealing” effect provided by Joule heating.

Compared with organic materials for OLEDs, perovskites are far more sensitive to the chemical and physical environments of the interfaces and therefore interface stability forms a critical issue for PeLED stability. For instance, the metal ions of Al electrode could easily diffuse through the carrier injection layer and chemically react with perovskites, leading to the decomposition of perovskites and undesirable modification of the charge injection layer.²⁰ Previous studies also revealed that the EL decay is much faster than the PL decay in PeLEDs,^{21,22} implying the serious potential issue of interface decomposition between the perovskites and carrier injection layer. For example, the deprotonation of organic cation by electron transporting-layer ZnO, may result in the degradation of MAPbI₃ and FAPbI₃ (**Section 4.1**) Therefore, selecting suitable interface materials, electrodes and the suppression of harmful interfacial reactions are critical for improving the operational stability of PeLEDs.

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4

Perovskite Emissive Layer Modulation

Perovskites possess excellent optoelectronic properties, promising for next-generation lighting and display applications. However, due to the lack of comprehensive investigations and in-depth understanding of perovskite crystallization and material properties, rational modulation of the perovskite emissive layers towards highly efficient and stable PeLEDs remains a big challenge. Combined (or synergistic) effects of material compositions, additives, and underlying interface layers play a crucial role in the crystallization of highly emissive perovskites. In this chapter, we will introduce some commonly used modulation approaches for high-quality perovskite emissive layers for PeLEDs.

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4.1 Composition engineering

The perovskite adopts a chemical formula of ABX_3 and its chemical stoichiometry (composition ratios of different cations and halide anions) could be altered, offering a great opportunity for composition engineering.

Composition engineering provides an important way to modulate the properties of obtained perovskite films to meet the requirements for various optoelectronic devices. As mentioned in **Sections 2.1** and **2.2**, such modulation can tune crystal structure (e.g., tetragonal vs. cubic systems) and the emission peak wavelength (or bandgap) of the perovskites from NIR to UV by partial or complete anion replacement. In addition, low-dimensional perovskites can be prepared by introducing large-size organic cations ($R-NH_3$) to substitute small-size A (MA, FA, or Cs) with different ratios in the precursor. The large-size cation, which serves as the spacer outside the layered perovskite, prevents the formation of 3D perovskites and results in mixed-dimensional perovskites. Due to the quantum confinement and/or passivation effects, the low-dimensional perovskite films show high PLQE even with low-intensity excitation.^{1,2}

4.1.1 Stoichiometric ratio control

Based on the ABX_3 formula, the precursor ratio of AX to BX_2 should be 1:1. However, during the annealing of perovskites, the lead halides may not be able to form complete ABX_3 coordination structures with organic cation salts due to the rapid crystallization process and sublimation or decomposition of organic halide salts (e.g., deprotonation reactions at the interfaces).³ All these can lead to the formation of vacancy defects and non-coordinated lead atoms. The halide vacancies with low formation energy could create a large density of shallow defects in the perovskites. Therefore, stoichiometric ratio control plays a crucial role in promoting film crystallization and reducing defect density in perovskites.⁴

In practice, increasing the ratio of AX to BX_2 can bring a series of benefits to the system. It can reduce the aggregation of components in perovskite precursors. For example, in $MAPbI_3$, with the excess MAI, PbI_2 tends to form complexes with decreased halogen-sharing degrees (or increased coordination numbers) from $[PbI_3]^-$, $[PbI_4]^{2-}$, $[PbI_5]^{3-}$, to $[PbI_6]^{4-}$ leading to smaller colloids in the precursor solutions.^{3,5} The resulting films present perovskite crystallites with small grain sizes and the existence of residual PbI_2

will be largely suppressed. In addition, excess AX can accumulate around the perovskite grains to passivate defects of surface and grain boundaries, leading to an enhanced PLQE.⁴ **Figure 4.1** exhibits influences of excessive FAI on the perovskite film properties, including enhanced crystallinity, improved PLQE, and increased PL decay lifetime, with the increasing ratio of FAI to PbI_2 .⁴

Figure 4.1 | The effects of adding excessive AX in the precursor solution. a, Increased crystallinity. **b,** Enhanced PLQE. **c,** Increased PL decay lifetime. **d,** Improved scanning electron microscope morphology. The figure is reprinted from Reference⁴ with permission from Nature-Springer.

In addition to the above advantages, the excessive FAI in the precursor can reduce the formation energy of black phase FAPbI_3 , and a mild thermal annealing temperature of 100°C is sufficient to form a stable black-phase FAPbI_3 . Currently, FAI to PbI_2 ratio from 2:1 to 3:1 is widely used for the fabrication of high-performance NIR PeLEDs (also with ZnO/PEIE as the EIL).^{4,6–9}

As shown in **Figure 4.1d**, the film morphology varies with the excess FAI. The formed platelet structures are proven to be advantageous for enhancing the light out-coupling of PeLEDs. However, when the ratio is about or beyond 3:1, negative effects occur on the resulting films, including poor film coverage and reduced carrier transport properties. Perovskite grains are likely to be surrounded by abundant organic compositions, leading to high carrier injection barriers, and eventually the poor performance of PeLEDs. Hence, the precise

control of stoichiometry in perovskite precursors is necessary for optimizing material properties and device performance.

4.1.2 A-site cation control

In ABX_3 perovskites, the tolerance factor (t_f) is critical for the structure stability of perovskite materials, in which a t_f value between 0.89 and 1 is favorable for the cubic structure. Besides the strategy of mixed halogens as mentioned in **Section 2.1**, a stable perovskite structure can be obtained by introducing mixed cations (the effective radii $Cs^+ < MA^+ < FA^+$). Unlike mixed-halogen perovskites, the bandgap of the mixed-cation perovskites is less sensitive to the ratios of mixed halide ions. Compared to $MAPbX_3$, $FAPbX_3$ is relatively thermally stable. However, the black phase of $FAPbI_3$ is less thermodynamically favorable and can easily be transformed into the yellow phase in a humid environment at room temperature, owing to the large tolerance factor (>1) of $FAPbI_3$.^{10–12} In contrast, $CsPbI_3$ perovskites show outstanding thermal stability ($\sim 250^\circ C$) without the issues of chemical volatility of organic cations. In addition, $CsPbI_3$ shows excellent optoelectronic properties, including large electron mobility, and low exciton binding energy (~ 35 meV).^{11,13} However, the black phase $CsPbI_3$ is unstable due to its small tolerance factor (e.g., the factor of $CsPbI_3$ is not within the 0.89–1.0 range), which is a disadvantage compared with hybrid perovskites.¹⁴

Considering all the above situations, mixed monovalent cation perovskites would be a suitable option to develop a stable perovskite structure with desired tolerance factor and desired properties. This approach has been proven successful in perovskite solar cells and also gained lots of attention in PeLEDs.^{15,16} Some early studies indicated that partial substitution of FA^+ or MA^+ with Cs^+ could alter lattice parameters and decrease the defect density, forming a stable perovskite phase and enhancing the brightness and EQE of the resulting PeLEDs. For instance, Zhang *et al.* showed that PeLEDs based on $FA_{(1-x)}Cs_xPbBr_3$ ($x=0.2$) on PEDOT:PSS/TFB presented a much higher brightness ($55,005\text{ cd}\cdot\text{m}^{-2}$) and EQE (2.8 %) compared with the PeLEDs with pure monovalent cation perovskites ($8563\text{ cd}\cdot\text{m}^{-2}$ and 0.6 %). With a further increase in the proportion of Cs^+ ($x > 0.2$), the device performance exhibits a significant decrease, which was attributed to the formation of impurity phases like Cs_4PbBr_6 and $CsPbBr_3$. To increase the proportion of Cs^+ , a large amount of CsBr is required in the precursor solutions and this can increase the impurity contents in the final films, which may increase the defect density and reduce the PLQE of the films.¹¹

In our study (**Paper 2**), we found that further increasing the ratio of Cs to FA can produce pure perovskite phase, instead of impurities, with the assistance of ZnO underlying substrate. In the perovskite preparation process, FAPbI₃-rich perovskite phase is formed at the initial stage due to its relatively lower formation (crystallization) energy. Later, ZnO could deprotonate FA⁺ and promote the cation exchange process between FA⁺ and Cs⁺, resulting in an effective substitution of FA⁺ by Cs⁺ and the formation of pure FA-Cs perovskite phases. Therefore, the fabricated PeLEDs possess tunable emission peak wavelengths from 715 nm to 800 nm by altering the FA to Cs ratio, demonstrating the maximum EQEs of above 15 %.

4.2 Additive engineering

Although compositional engineering is an efficient way to control the crystallinity and the optoelectronic properties of perovskite films, their modulation effects are rather limited. Additives engineering is demonstrated to be another effective and widely utilized strategy to fabricate high-performance PeLEDs. Additives can be introduced into the perovskites mainly by two methods, either direct introduction into perovskite precursor solutions or indirect ways where additives are dissolved in anti-solvent and the anti-solvent dripping is applied during the spin-coating of perovskite films.

In this part, we will focus on three key functions of additive engineering in perovskites, namely, defect passivation, molecular interaction, and modulation of crystallization kinetics.

4.2.1 Defect passivation

High defect density in perovskites poses an intrinsic threat to the efficiency and operational stability of PeLEDs due to its effects in increasing nonradiative recombination and severe ion migration issues.

Lewis bases/acids are a class of commonly used passivation additives for perovskites. The unbonded electron pair of Lewis bases could form coordination with exposed Pb²⁺ originated from halide vacancies. Typical examples for this class are trioctylphosphine oxide (TOPO), thiophane, and pyridine due to the electron-donating capability of P, O, S, and N atoms in these materials.^{17,18} With these additives, the defect density of perovskites can be largely reduced, and the PLQE and carrier lifetime can therefore be

increased. Organic molecules possessing functional groups of -NH_2 , and -COOH , can also effectively passivate defects of perovskites. These molecules include poly(ethylenimine) [PEI], 1,11-diamino-3,6,9-trioxaundecane (ODEA), 5-aminovaleric acid (5-AVA), 2,2'-(ethylenedioxy)bis(ethylamine) [EDEA], adipic acid (AAC), and pimelic acid (PAC), and their chemical structures are displayed in **Figure 4.2**.^{8,9,19,20}

Figure 4.2 | Chemical structures of typical additives.

Recently, Xu *et al.* revealed that the capability of additives in forming hydrogen bonding with FAI can influence the passivation effects. In the study, introducing O atom in the alkyl chain of a diamino-functionalized additive can weaken its hydrogen bonding formation capability with FAI. Through this modification, utilizing additive ODEA can improve the NIR PeLEDs with a maximum EQE of 21.6 %.¹⁹

Figure 4.3 | Schematic illustration of perovskite defects passivation by alkali metal halides. The cross-section of a perovskite film (crystals) is shown. For the passivation, the vacancies can form coordination with halides while the halide defects in perovskite can form benign compounds with alkali metal ions (K^+). The figure is reprinted from reference²¹ with permission from Nature-Springer.

Besides organic additives, their inorganic counterparts can also be used for defects passivation of perovskites, such as alkali metal halides (e.g., KX and

RbX).²¹ According to Goldschmidt tolerance factor (**Section 2.1**), the alkali metal K and Rb atoms are too small to fit into the perovskite lattices and therefore tend to aggregate at the perovskite surfaces and grain boundaries to passivate the halogen vacancies (**Figure 4.3**). Since these additives contain small-sized cations, carrier transport properties can be less affected. However, when alkali metal halides are excessive, serious aggregation at the grain boundaries can form and severely hinders the effective transport paths of carriers.²¹

4.2.2 Effect of Molecular reaction

Besides passivation, the chemical reaction might be introduced by organic additives, of which the functional passivating moieties (such as -NH₂, -COOH, -COOR) are chemically active and can initiate typical chemical reactions. The probability of molecular reaction can further be increased with the various combinations of reactive organic cations of perovskite, multi-functional groups of additives, and interlayers.^{8,9,22–24} In addition, employing certain metal oxides as interlayers could even bring catalysis effects for some molecular reactions.^{9,25} The additives could even react with themselves during the perovskite crystallization, such as cross-linking.^{20–22}

Compared with additives forming weak molecular interaction (such as hydrogen bonding), additives for molecular reactions can provide more beneficial effects for perovskites, resulting in optoelectronic devices with improved operational stability. The stability improvement in devices could be ascribed to effects such as the suppressed interfacial reaction, elimination of reactive organic ingredients, and chemically anchoring to perovskite surfaces and grain boundaries with network molecules.^{8,9,22–24}

In fact, different additives could induce different molecular interactions, and this could lead to significant differences in the operational stability of the PeLEDs. Indeed, although PeLEDs with different additives could achieve similar EQEs, drastic differences exist regarding their operational stability (half-lifetimes).^{8,9,19} As **Table 5.1** presents, it can be seen obviously that PeLEDs using 5-AVA and ODEA exhibit very similar EQEs but remarkably different operational stability. It was revealed that the amidation reaction between 5-AVA and PEIE is the main reason behind the excellent operation stability of PeLEDs treated by 5-AVA. In the study, Cao *et al.* claimed that such a reaction can form an insulating layer between ZnO and perovskites, resulting in suppressed interfacial reaction and improved device stability.⁸

In our study (**Paper 3**), we found that amidation reactions between excessive FAI and additives possessing carboxylic acid groups can occur and transform these reactive FAI into stable amides with the catalysis of the electron transport layer ZnO. As a result of suppressed harmful interfacial reactions, the device stability is significantly improved with T_{50} of the resulting PeLEDs (PAC as the additive) approaching 700 hours (more details in **Section 6.3**).

The molecular reactions introduced by additives are complex, where more detailed investigations are desired for further improvements of the device stability.

Table 5.1 | Device performances of NIR PeLEDs with different additives. The data are collected from reference.^{8,9,19}

Additive	EQE	T_{50} lifetime
5-AVA	20.3 %	20 hours @ 100 mA·cm ⁻²
ODEA	21.6 %	20 hours @ 25 mA·cm ⁻²
AAC	17.8 %	189 hours @ 20 mA·cm ⁻²
PAC	18.6 %	682 hours @ 20 mA·cm ⁻²
EDEA	17.6 %	25.6 hours @ 20 mA·cm ⁻²

4.2.3 Perovskite crystallization modulation

In addition to the defect passivation and the effect of molecular reaction mentioned above, some additives can form coordinate bonds with lead ions and modulate the crystallization of perovskites.

It has been found that additives containing more than one electron-donating function moieties can form chelates with Pb²⁺ in the perovskite precursor solution.^{7,8,26,27} Therefore, the lead-additive intermediate phase can be formed during the spin-coating process, and halides are possible to replace the additive during the annealing process to form high-quality perovskites. This lead-additive intermediate phase raises the activation energy for perovskite nucleation and slows down the crystallization rates, resulting in the reduction of the vacancy defect density in perovskite film and the improvement of PLQE. However, low-dimensional perovskites or non-perovskite phases can emerge easily if the coordination affinity between the additive and the perovskite components is too strong. These negative effects are expected to be detrimental to the device performance, especially device stability, of the

resulting PeLEDs. It is also a quite common issue since most of the effective additives are amine and its derivatives.^{8,19,26}

In our study (**Paper 4**), we demonstrated that the negative effect of additives can be eliminated by introducing a combination of two types of additives (diamine and triacrylate), among which molecular reaction proceeds with the assistance of ZnO. The combined additives can weaken the chelate effect of lead-additive intermediate phases and prevent the aggregation of PbI_2 , leading to the improved perovskite crystallization with preferred orientation. By the crystallization modulation, the obtained perovskite emissive layers show reduced trap-mediated non-radiative recombination and the obtained PeLEDs exhibit high EQEs (23.8 %) and outstanding stability (T_{70} lifetime of 290 hours @ 20 $\text{mA}\cdot\text{cm}^{-2}$).

4.3 Interface engineering

In a typical PeLED (**Figure 3.1**), the perovskite emissive layer is sandwiched between the EIL and the HIL. The charge carrier injection is largely affected by the interlayer, which is critical for the device performance of the resulting PeLEDs (**Section 3.3**). In addition, the perovskite has to be deposited on top of either EIL or HIL in the device fabrication process. The surface properties of the underlying layers can thus largely affect the film crystallization process and the properties of formed perovskites. In some specific cases, chemical reactions occur at the interface and could be utilized to modify the properties of perovskite. In this thesis, we used ZnO-PEIE as the underlying “substrate” (or EIL) for perovskite deposition. Herein, we will briefly discuss the influence of the interfacial layer and the properties of ZnO on the modulation of the perovskite emission layer to achieve high-performance PeLEDs.

4.3.1 Effect of interface

Perovskite is quite sensitive to the physical and chemical properties of the interface. The interfacial layers can affect the morphology, crystallization, and defect concentration of perovskite deposited on the top of it.²⁸ Generally, a hydrophilic interface will form a more continuous perovskite layer, and this property can be acquired by surface treatment or additional modification layer.²⁷⁻²⁹ For example, the introduction of PEIE or PEI between substrate ZnO and perovskite improves the wettability of the surfaces and passivate surface defects of ZnO, resulting in improved crystallinity and morphology and greatly

improved device performance.^{28,30} Cho *et al* demonstrated that introducing a buffer layer (perfluorinated ionomer) increases the nucleation sites during crystallization.²⁹ The deposited CsPbBr₃ perovskite is highly uniform on the PEDOT:PSS layer which was modified with perfluorinated ionomer molecule.²⁹

In addition to the important influence of physical properties on perovskite growth, the chemical properties of the interfacial layer can also affect the stability of materials and devices (e.g., the deprotonation of organic cations by the underlying layer ZnO). This kind of interfacial reaction can cause much faster EL decay than PL decay in the operating PeLEDs.^{8,9} Inserting an insulating layer between ZnO and perovskite, can greatly suppress the detrimental interfacial reaction and hence enhance devices stability.

4.3.2 Properties of ZnO interlayer

ZnO, widely known as a third-generation semiconductor, possesses a wide bandgap of about 3.4 eV.³¹ It is highly transparent in visible spectrum, and demonstrates a high electron mobility, making it promising as a charge transport layer in optoelectronic devices, as demonstrated in previously reported organic and quantum dot-based devices.^{32,33} As shown in **Figure 3.5**, the valence band maximum of ZnO is located at a relatively deep energy level and therefore effectively promotes the extraction of electrons from perovskite while prevents holes from diffusing towards cathode in a perovskite solar cell. However, ZnO as the electron transport layer in perovskite solar cells usually demonstrates relatively poor device performances (both device efficiency and stability), compared with other metal oxide interlayers (*i.e.*, SnO₂ and TiO₂).^{34,35}

It was found that ZnO could promote the proton transfer reaction at the ZnO/perovskite interface, where the organic cations (e.g., FA⁺ and MA⁺) will be deprotonated.²⁸ Such a process results in easy decomposition of the perovskite during the thermal annealing. The alkalinity of the interface (ZnO > TiO₂ > SnO₂) determines the efficiency of the deprotonation of the organic cations.^{4,28} In addition, the residual hydroxyl groups and acetate ligands on the surface of ZnO nanocrystals, will accelerate the above reactions at the interface especially under elevated temperatures, leading to rapid thermal decomposition of the perovskites during the annealing process.²⁸

The details of the above processes could be illustrated utilizing MAPbI₃ deposited on ZnO as an example (schemes in **Section 4.1** and **4.2**). These reactions therefore indicate the reasons of the instability and degradation of perovskites on the ZnO surfaces.³⁴ Compared with MAPbI₃, FAPbI₃-based devices are more stable on the ZnO due to the more difficult deprotonation of FA⁺ and the less volatile nature of the FA.⁵

Yuan *et al.* explored these processes by comparing the crystallization process of MAPbI₃ on SnO₂, TiO₂, and ZnO surfaces with vacuum processing instead of thermal annealing.²⁸ It was found that perovskite films deposited on ZnO presented high crystallinity while SnO₂ and TiO₂ inhibited crystallization. This indicated without external energy provided by thermal annealing, the above interfacial reaction (**Section 4.2**) is difficult and the ZnO surfaces are therefore beneficial for perovskite crystallization.²⁸ It was later revealed that the deprotonation process of organic cations in FAPbI₃ by ZnO is the key to deposit high-quality perovskites. Such a process enables the effective conversion of the perovskite precursor mixtures (*i.e.*, FAI and PbI₂) into pure and high-crystallinity perovskites (**Paper 1**).⁴ As mentioned above the modifying layer (such as PEIE or PEI) between ZnO and perovskite, can also modulate the deprotonation capability of ZnO.^{28,30} In addition, the residual acetate ligands remaining on the surface of ZnO nanocrystals reduce the activation energy for perovskite crystallization.²⁸

Besides the deprotonation of organic cation, the alkaline ZnO can act as a catalyst or activator in some organic reactions, *e.g.*, the amidation reaction between carboxylic acids and amines. It increases the probability of chemical reaction between multi-functional organic groups, which could come from additives, organic cations in perovskites, and other organic molecules in the devices. The inert environment of perovskite and significantly improved device stability of the PeLEDs can be achieved by rational design and precise control of molecular reactions (**details in Section 4.2**).

To sum up, ZnO as the EIL of PeLEDs can not only deprotonate organic cation and lower the activation energy to promote the perovskite crystallization but also can serve as a catalyst for some molecular reactions to provide a more inert environment for perovskite. Benefited from these unique properties, PeLEDs with high efficiency and excellent operational stability can be achieved with a careful modulation of the surface properties of ZnO.

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5

Methods and Characterizations

In this chapter, we will move to the experimental techniques of perovskite preparation, device fabrication, and key characterization techniques that are utilized in this thesis.

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5.1 PeLED fabrication

In this thesis, we adopt the *n-i-p* configuration of PeLEDs (**Figure 3.1**) and fabricate the device based on the standard procedure as detailed below:

1. **ITO-coated substrate cleaning.** The ITO substrates are washed by detergent, and boiled with TL1 solution (a mixture of H_2O , H_2O_2 , and NH_3

with a volume ratio of 5:1:1) for 15 min sequentially. After the substrates are dried with N_2 flow, they are treated by UV-Ozone for 15 min for further use.

2. **EIL deposition.** In this thesis, we mostly use ZnO/PEIE for EIL. The above substrates are spin-coated by ZnO nanoparticles solution at a spin speed of 4000 rpm for 30 s in air. Then, the substrates are transferred into a N_2 -filled glovebox and spin-coated by a thin layer of PEIE (0.05 wt%, dissolved in isopropanol) at a spin speed of 5000 rpm for 30 s. The obtained samples are thermally annealed at 100 °C for 10 min and slowly cooled down to room temperature.
3. **Perovskite film deposition.** Perovskite precursors are prepared by dissolving FAI:PbI₂:additive in dimethylformamide (DMF) with a molar ratio of $x:1:y$, where x varies between 1 and 3 and y varies between 0 and 0.6. For certain cases of additives, the optimized concentration of PbI₂ would be different. All precursor solutions are stirred at 50 °C for 2 hours and then spin-coated on the above samples at a speed ranging from 4000 to 6000 rpm for 25 s, followed by thermal annealing for 10 min at 100 °C.
4. **HIL deposition.** We deposit TFB by spin coating its chlorobenzene solution (12 mg/mL) onto the perovskite films at 3000 rpm for 30 s.
5. **Anode deposition.** Before thermal evaporation, all substrates are covered by shadow masks with well-defined electrode shapes. We normally deposit MoO_x and metal electrodes (Ag or Au). The active area of the device (overlapped part of anode/cathode) is 7.25 mm².

The ZnO NPs utilized for EIL can be prepared *via* a solution precipitation method reported by our previous study.^{1,2} Briefly, 1.5 mmol Zn(Ac)₂·2H₂O is dissolved in 15 mL dimethyl sulfoxide (DMSO) with stirring at 30 °C. 2.8 mmol tetramethylammonium hydroxide pentahydrate (TMAH·5H₂O) in 5 mL ethanol is then added in the above solution. The mixture is kept stirring for 24 hours before the precipitation process. Ethyl acetate is used to precipitate the ZnO NPs, and the obtained precipitants are re-dispersed in ethanol. This precipitation process is repeated twice and the finally obtained ZnO NPs are re-dispersed into ethanol (8 mL) and filtered with a 0.45 µm PTFE filter for further use.

With the above procedure, we can fabricate PeLED and characterize its performance. In the following sections, we will focus on characterizing the properties of perovskite films (prepared from Step 1 to 3).

5.2 Optical characterizations

In this section, we will briefly introduce key equipments and techniques for the study in this thesis, including absorption and photoluminescence characterizations.

5.2.1 UV-Vis spectrophotometer

UV-Vis-NIR spectrometer is utilized to characterize the transmission of the materials. The transmission of the materials (T) can be converted into the extinction (E) of the materials, which is the sum of the absorption (A) and the reflection or the scattering (R) for non-smooth surfaces:

$$T = 1 - E = 1 - A - R \quad (\text{Eq 5.1})$$

Normally, the absorbance (Abs) is utilized and it can be calculated by:

$$Abs = \log_{10} \frac{1}{T} = -\log_{10} T \quad (\text{Eq 5.2})$$

Figure 5.1 | Schematic illustration of a UV-Vis-NIR spectrophotometer.

The typical set-up for the equipment is shown in **Figure 5.1**. Briefly, the light from the source is dispersed into monochromatic light by a prism or a grating for each measurement. The monochromatic light is splitted into two beams which travel through the sample and the reference, and the transmitted intensities (I and I_0) are collected by detectors. Using the two quantities, the transmittance at this certain wavelength is:

$$T = I/I_0 \quad (\text{Eq 5.3})$$

It should be noted that it is different from fiber spectrometer, where T at different wavelengths are recorded simultaneously by a CCD detector. UV-Vis-NIR spectrophotometer is preferred for many cases since it can provide

high sensitivity, low noise-signal ratio, and could eliminate large variations of light intensity at different wavelengths.

In the thesis, we used UV-Vis-NIR spectrophotometer to estimate the bandgap of the perovskites, identify different components in perovskite, and compare the crystallization kinetics between different additives.

5.2.2 Fourier-transform infrared spectrometer

Similar to UV-Vis-NIR spectrophotometer, Fourier-transform infrared spectrometer (FT-IR) is specifically designed for material transmission (or absorbance) characterization in the infrared range (usually 2 μm to 30 μm). Different from the dispersion method used in **Section 5.2.1**, FT-IR records all data simultaneously via interferograms (time-domain) and applies certain mathematic algorithm (*i.e.*, Fourier transform) to convert them into frequency-domain spectra.³

A schematic illustration of the equipment set-up is displayed in **Figure 5.2a**. The core part of FT-IR is the Michelson interferometer, which can produce interferogram by tuning the optical path difference between two identical light beams (separated from a beam-splitter). The adjustment could be achieved by the combination of a fixed mirror and a movable mirror, which is controlled by a linearly translational stage. The obtained interferogram by a collection of optical path differences (time-domain) can thus be translated into frequency-domain absorbance spectra.

Figure 5.2 | Schematic illustration of a FT-IR (a) and ATR set-up (b).

The set-up in **Figure 5.2a** is designed for IR-transparent samples. For bulk materials, thick films, or films desposited on IR-opaque substrates (*e.g.*, glass),

we can use the attenuated total reflection (ATR) accessory of FT-IR (**Figure 5.2b**). In this set-up, the material is placed on top of a ATR crystal (normally diamond). Due to the drastic difference in the refractive index, total internal reflection occurs at the interface between the film and the ATR crystal. The evanescent wave generated by the total internal reflection propagates at the interface and can be absorbed by the film, reducing the measured intensity of reflected light. With these, we can then obtain its absorbance (transmission) spectrum.

It should be noted that the absorbance or transmission spectra obtained in this ATR set-up have a strong dependence on the penetration depth (ξ) of the evanescent wave at the wavelength λ :³

$$\xi = \frac{\lambda \cdot n_1}{2\pi \sqrt{\sin^2 \theta - n_2^2/n_1^2}} \quad (\text{Eq 5.4})$$

where n_1 and n_2 are the refractive indices of ATR crystal and sample, and θ is the incident angle of light in the ATR crystal.

FT-IR is a fast measurement approach and provides accurate, precise, and high-resolution spectra. The IR absorption spectra are highly useful in identifying the functional groups, covalent bonds, and analyzing some molecular interactions between perovskites and additives. In this paper, we mostly used a Vertex 70 FT-IR spectrometer (Bruker) and a PIKE MIRacle ATR accessory (a diamond prism as ATR crystal).

5.2.3 Photoluminescence quantum Efficiency

The basics of PLQE have been introduced in **Section 2.2.5** and in this part we will introduce its characterization set-ups. In order to ensure that all the emitted photons are collected, we normally utilize an integrating sphere coupled with a spectrophotometer. The wall of integrating sphere is coated with a layer of white reflective materials enabling us to collect the intensities of both excitation laser (herein, 450 nm continuous laser source) and emission light (herein, around 800 nm). For accuracy, the detected intensity of the system is required to be calibrated by a standard light source.

The procedure of a typical measurement in this thesis is:

- Firstly, the blank spectra of the laser intensity $S_A(\lambda)$, and emission intensity $E_A(\lambda)$, are collected with no devices in the sphere. Both 1 and 2 positions

in the set-up (see **Figure 5.3**) are occupied by two blank substrates as references.

- Secondly, the blank substrate at position 1 is replaced by the test device. The laser $S_B(\lambda)$ and emission spectra $E_B(\lambda)$ are collected.
- Thirdly, place the blank substrate at position 1, test the device at position 2, and record the laser $S_C(\lambda)$ and emission spectra $E_C(\lambda)$.
- Finally, we can calculate the PLQE by:

$$PLQE = \frac{(E_B - E_A)S_C - (E_C - E_A)S_B}{(S_C - S_B)S_A} \quad (\text{Eq 5.5})$$

Figure 5.3 | Schematic illustration of a typical set-up for PLQE. In the top panel, the measurement steps in an integrating sphere is shown. In the bottom panel, both the laser and emission spectra are displayed schematically. The red colour represent sample.

5.2.4 Time-correlated single-photon counting

Time-correlated single-photon counting (TCSPC) is often employed to study the charge carrier dynamics in semiconductors. The typical set-up for the measurement is exhibited schematically in **Figure 5.4**.

Figure 5.4 | Schematic illustration of a typical set-up for TCSPC.

In the TCSPC measurements, laser pulses with certain repetition rate (0.1-10 MHz) and duration (below 100 ps) are used. A beam splitter is employed to split the laser into two parts: one to excite the fluorescence of the sample while the other to trigger the timing electronic circuits to start to count the time. The photodetector (mostly photomultiplier tube) in the optical path of sample can collect the signal of a single photon and stop the time counting. Since the laser pulses we used have a high repetition rate, we can repeat the same process for millions of times and have the histogram of the photon counts by time difference (or time after the pulse excitation, see **Figure 5.4**), which is the TCSPC curve.

The intensity of the laser pulses can also be modulated by an attenuator and thus we can measure the light intensity-dependent TCSPC. In this thesis, we used a FLS 1000 (Edinburgh Instruments) to collect TCSPC curves.

To analyze the TCSPC data, we normally fit the curve (counts I) with a quadratic exponential equation (starting at time t_0):⁴

$$I(t) = I(t_0) + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (\text{Eq 5.6})$$

where t is time, τ_1 , τ_2 are the lifetimes of fast and slow recombination, and A_1 and A_2 are their corresponding amplitudes. Besides τ_1 and τ_2 , we can also calculate the average lifetime (τ_{average}) of the whole system:

$$\tau_{\text{average}} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \quad (\text{Eq 5.7})$$

5.3 Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is a well-established technique for determining the chemical structures of organics, reaction states and dynamics, and chemical environment of molecules.⁵

NMR can be regarded as an optical characterization method, although its frequency range [60 - 1000 MHz, or radio frequency (RF)] is far lower than the visible. The simplified schematics of a NMR set-up is shown in **Figure 5.5a** and the equipment is operating within a magnetic field.

Figure 5.5 | Schematic illustration (a) and working principles (b) of NMR.

The working principle of NMR is based on the magnetic-field induced splitting of energy levels of nuclear spin energy levels (Zeeman splitting). As shown in **Figure 5.5b**, the generated energy gap (corresponding to its Larmor frequency) within the magnetic field is located in the RF range and depends on the magnetic field intensity. For example, in **Paper 3**, a magnetic field of 11.7 T gives the frequency for ^1H spectra of 500.180 MHz. By measuring the changes of RF wave absorption, we can obtain the NMR spectrum of the materials.

The main information that can be obtained from a NMR spectrum are:

- **Chemical shift.** Since the nucleus could locate in different chemical environments, and therefore the real energy gap shows deviation from the ideal case. And this shift of the Larmor frequency is defined as the chemical shift (δ_{ppm}) of the nucleus:⁵

$$\delta_{ppm} = 10^6 \times \frac{\nu_{sample} - \nu_{reference}}{\nu_{reference}} \quad (\text{Eq 5.8})$$

where ν_{sample} is the measured Larmor frequency, and $\nu_{reference}$ is the Larmor frequency of a standard reference (e.g., tetramethylsilane or TMS), whose absorption frequency is set as 0 ppm. The chemical shift could be affected by nearby electronegative atoms (e.g., O, N, or halogen) and unsaturated groups (e.g., C=C, C=O, or aromatic). For example, in the inset of **Figure 5.5a**, the ^1H signal of ethanol has three peaks in the chemical shift due to three types of environment (marked by different colours).

- Integration intensity. It is associated with the number of (equivalent) nuclei leading to this peak. For example in **Figure 5.5a**, ^1H in green shows the highest intensity due to three equivalent ^1H in ethanol.
- Splitting. It refers to the formation of multiple closely-packed peaks as indicated by ^1H in green (triplet) and blue (quartet) in **Figure 5.5a**. This is originated from the influence of neighbouring nuclei and the number of peak splitting is $N+1$ in general, where N is the number of ^1H on the adjacent atoms. For example, in ethanol molecule shown in **Figure 5.5a**, for green ^1H , the neighbouring carbon atom has two ^1H , and therefore the green ^1H peak exhibits triplet splitting.

The above information forms the fundamentals of NMR spectra analysis, where more information can be available by further exploration. In this thesis, we studied the NMR spectra to understand the detailed molecular interaction between perovskite components and additives (**Paper 3**).

5.4 Microstructural characterizations

The microstructures of perovskite thin films can significantly affect the film quality (e.g., crystallization, defect density) and light out-coupling properties. Herein, we will focus on the techniques that provide us with an overall evaluation of film quality, such as crystallite (grain) sizes, orientation, and morphology.

5.4.1 Scanning electron microscopy

Scanning electron microscopy (SEM) produces high-resolution images of samples with magnification rate beyond the optical microscope. SEM utilizes a beam of focused electrons (primary electrons) to scan sample surface and collects the stimulated signals from the surface. The signals can be secondary electrons, Auger electrons, backscattered electrons, cathodoluminescence, and X-rays (see **Figure 5.6**).

The primary electron beam can hit the core electrons of the atoms at the surface and emit the secondary electrons (**Figure 5.6b**). These electrons with low energies could be collected by the electron detectors and used for surface imaging in most cases. The intensity of collected secondary electrons is dependent on the microstructures of the surface and thus it can provide detailed information on the surface morphology.

Figure 5.6 | Working principles of SEM (a) and the formation of different signals in SEM (b).

In addition to secondary electrons, the X-ray emitted due to the energy level transition from outer orbitals to inner orbitals (bottom right panel in **Figure 5.6b**) can provide detailed chemical (elemental) information of the surface. Energy dispersive X-ray (EDX) spectroscopy, a part that normally integrated with a SEM, is designed to collect the X-ray signals.

In this thesis, we used SEM and EDX to characterize the nanostructures and elemental distribution of perovskite thin films (nano-platelets).

5.4.2 X-ray diffractometry

We normally use X-ray diffractometry (XRD) to characterize the crystal structures of perovskite films. The working principles of XRD is based on the Bragg's law, which can be written as:

$$2d \cdot \sin\theta = n \cdot \lambda \quad (\text{Eq 5.9})$$

where d is the inter-distance between two neighbouring crystal planes, θ is the incident angle of the X-ray, λ is the wavelength of the X-ray, and n is an integer number (1, 2, ...). The law can be derived from the optical path difference of two X-ray beams to produce constructive interference, as shown in **Figure 5.7**.

Using XRD, we can obtain rich information on the film, including the crystal structure of the materials (crystal system, point group, and space group), the

components in the films (different phases), and crystal size. The crystal or grain size (L) of the materials could be estimated via the Scherrer equation:

$$L = \frac{K \cdot \lambda}{B \cdot \cos \theta} \quad (\text{Eq 5.10})$$

where K is the shape factor of crystallites (e.g., 0.94 for spherical crystal with cubic symmetry), and B is the full width at half maximum (FWHM) of the diffraction peak in XRD spectrum (intensity vs. 2θ).

Figure 5.7 | Schematic illustration of the Bragg's law.

5.4.3 Grazing incidence wide-angle X-ray scattering

Although XRD can provide useful information on crystalline structures of the films, the detailed information on the spatial distribution of these crystallites (e.g., their orientations) is still absent. These information can be obtained via grazing incident wide-angle X-ray scattering (GIWAXS).

Figure 5.8 | Schematics of the grazing incident X-ray-based characterizations. The figure is reprinted from Reference ⁶ with permission from John Wiley and Sons.

As shown in **Figure 5.8**, a beam of high-intensity (also high-energy) X-ray irradiates the film surface at a grazing incident angle (α_i) and all the scattered light signals are collected by a two-dimensional detectors. The obtained results are normally plotted in a two-dimensional heat map as shown in the insets of **Figure 5.8**, which directly reflects the information of the reciprocal space of the crystalline structures in the film. Based on the distance between the sample and the detector, the techniques can be named as GIWAXS or grazing incident small-angle X-ray scattering (GISAXS). To investigate the nanostructure and microscale morphology (orientations of crystallites) of the film, GIWAXS is preferred.

Figure 5.9 | Analysis principles of GIWAXS. Based on the scattering spots in the scattering spectra, the orientations of crystallites and their respective fractions can be calculated by area integration. The figure is reproduced from Reference ⁷ under the terms of the Creative Commons CC-BY license.

Figure 5.9 exhibits the basic principles on analysis of GIWAXS spectra. Briefly, the orientation angles of crystallites can be associated with their positions (scattering spots) in the spectra. For instance, (010) plane in face-on (or horizontal) orientation is located in the q_z axis (q is reciprocal of distance, $q = 2\pi/d$), while it is positioned at the q_{xy} axis for edge-on (or vertical) orientation. Converting the 2D spectra at a constant q_r ($q_r = (q_{xy}^2 + q_z^2)^{1/2}$) into 1D spectra, we can calculate the fractions of different orientations by integrating the area size within different scattering peaks (corresponding to spots in the 2D spectra).

In this thesis, GIWAXS measurements were performed on the NCD-SWEET beamline, ALBA Synchrotron, Spain. As presented in **Paper 4**, we employed the GIWAXS to probe the microstructures (crystallites orientations) of the perovskites modulated by different additives.

5.5 References

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6

Summary and Outlook

The main goal of this thesis is to develop and understand efficient and highly stable NIR PeLEDs by modulation of perovskites. In this chapter, we briefly review four appended papers and present a concise outlook for future studies.

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6.1 Paper 1

Title: ***Unveiling the synergistic effect of precursor stoichiometry and interfacial reactions for perovskite light-emitting diodes***

With great efforts made during the past few years, EQE of NIR PeLEDs is now above 20 %, approaching those of the commercial devices. Previous studies have mainly focused on improving the quality of the perovskite emissive layer by employing methods including modulation of precursor composition, crystal dimensionality, and the introduction of various additives to passivate defects. However, few studies have been dedicated to the underlying interlayers, which can largely affect the perovskite crystallization. In addition to this, interfacial reactions between precursor components and the bottom interlayers possibly introduce various uncertainties to the overall device performance. Therefore, it is necessary to gain an in-depth understanding of the combined effects of interfacial properties and precursor stoichiometry on the properties of perovskite films.

Figure 6.1 | Schematic illustration of perovskite crystallites growth on different underlying interlayers (ZnO, SnO₂, and TiO_x) before (a, b) and after thermal annealing (c, d, e). The figure is reprinted from Reference¹ with permission from Nature-Springer.

In this paper, we studied the perovskite films and PeLEDs based on three widely used EILs (ZnO, SnO₂, and TiO_x, modified with an ultra-thin layer of PEIE) as shown in **Figure 6.1**. We presented that the radiative recombination of perovskite films can be remarkably enhanced by introducing excess organic

cations into the precursor, leading to highly emissive perovskites and high-efficiency PeLEDs. It was revealed that ZnO can efficiently deprotonate the excess organic cations and promote the formation of high-quality perovskites from precursor intermediates.

6.2 Paper 2

Title: **High-performance near-infrared perovskite light-emitting diodes with fine-tuning emissions**

Figure 6.2 | Cation exchange and perovskite crystal growth. Illustration of cation exchange and film growing process on ZnO/PEIE substrates (a). PL peak positions of perovskite films with different amounts of CsI during the thermal annealing process (b). UV-vis absorption and steady-state PL spectra (c). XRD spectra of the annealed films with different amount of CsI (d).

PeLEDs with emission peaks located in the NIR range hold great promises for biomedical research. For applications like subcutaneous deep-tissue illumination and heart rate monitoring, a precise and accurate control of light generation and transmission with various wavelengths is required.² This places a new challenge for PeLEDs since tuning the wavelength of emission light might lead to the instability of the devices. For example, mixing monovalent cations (e.g., modulating the ratio of Cs to FA) is a promising

strategy to improve the emission tunability. However, non-perovskite phases can form upon elevating the Cs to FA ratio, resulted from the differences in formation energy of pure FAPbI₃ and CsPbI₃ phases.³ Therefore, it is challenging to obtain Cs-FA perovskite emitters with stable and fine-tuning emissions.

In this paper, we found out that the deprotonation process initiated by ZnO efficiently promotes the Cs-FA cation exchange during thermal annealing and the formation of pure phase Cs-FA perovskite (see **Figure 6.2**). This enabled the fabrication of perovskites with stable and easily tunable NIR emission, leading to high-performance NIR PeLEDs with peak EQE over 15 % in a wavelength range from 715 nm to 800 nm.

6.3 Paper 3

Title: ***Critical role of additive-induced molecular interaction on the operational stability of perovskite light-emitting diodes***

In addition to the EQE and emission wavelength of PeLEDs, which are the focus of the previous two studies, the device stability is also of critical importance for practical applications of PeLEDs. Currently, the operational stability of PeLEDs remains poor. Additive engineering is believed to be a promising method to enhance device efficiency and operational stability and has been widely used in photovoltaic devices. However, the understanding of the additive-perovskite interactions remains superficial and several critical problems remain unresolved, making it rather challenging to find out an effective and precise way to improve PeLED stability. For example, why do some additives enhance the EQEs of PeLEDs to the same level yet with significant difference on the operational half-lifetimes?

To solve the problem, we systematically studied molecular interactions between various additives and perovskite components in this study. We found that the amidation reaction between dicarboxylic acids (e.g., AAC) and FAI can consume the excess (and also chemically active) FA⁺ cations and convert them into inert amides, preventing a detrimental interfacial reaction. Thus, AAC-treated perovskite films exhibit excellent thermal stability and AAC-treated PeLEDs present greatly improved operational stability. Further optimization of amidation reaction with PAC as an additive, the operational

half-lifetime of PeLEDs approached 700 hours at 20 mA/cm² while maintaining a high EQE of 18.6% (**Figure 6.3**).

Figure 6.3 | Schematics of the molecular interactions between dicarboxylic acid (additive) and perovskite components. The figure is reprinted from Reference⁴ with permission from Elsevier.

6.4 Paper 4

Title: *Rational design of in-situ molecular reactions for highly efficient and stable perovskite light emitting diodes*

It remains a key challenge to achieve PeLEDs with excellent EQEs and device stabilities simultaneously. Generally, devices with high efficiencies present a relatively moderate operational lifetime, while the efficiency of highly stable PeLEDs remains less attractive. In this study, with the combination of two rationally selected additives (*i.e.*, diamine and triacrylate), we successfully eliminated the negative effect of commonly used diamine-based additives and obtained highly efficient PeLEDs with outstanding operational stability.

It reveals that the combination of the two additives and the precise control of molecular reactions can effectively modulate the perovskite emissive layers,

including the regulation of the crystallization direction, the passivation of defects, and the suppression of potential detrimental interfacial reactions. For example, the chemical reactions of the two additives can weaken the coordination affinity of lead-additives and improve crystallite orientation as well as improved crystallinity effectively decreases bulk defect density of perovskites, which can hardly be achieved by defect-passivating additives, and therefore enhances PLQE and device EQE. The resulting PeLEDs possess a peak EQE of 23.8% and excellent operational stability with a T_{70} lifetime of 290 hours at 20 mA/cm².

6.5 Outlook

The past several years have witnessed the rapid increase in EQEs of PeLEDs marching toward commercialization. However, the operational stability of PeLEDs remains the primary challenge for practical applications, for which the required minimum operational half-lifetime is 20000 hours.⁵ Thus, it is crucial to have a comprehensive and in-depth understanding of perovskite materials and devices to achieve PeLEDs with excellent operational stability and high efficiency. On one hand, we should understand and modulate the intrinsic properties of perovskite materials for optimal performance. On the other hand, we should precisely regulate and rationally integrate the emission layer and interfacial layers to enhance light extraction and suppress device degradation.⁶ Herein, we list several promising directions for future studies.

- Solving the instability issues of perovskites. For instance, a stable perovskite crystal structure (cubic phase) can be obtained *via* mixing halides or cations. In addition to this, defects passivation and crystallization regulation by certain additives can also be useful. It is expected that, with these strategies, the densities of bulk and surface defects, grain boundaries in perovskite can be effectively reduced and the ion migration can be largely suppressed.
- Precise control of interfacial reactions. During the operation of PeLEDs, the applied bias can electrically drive interfacial and intra-grain ion migration, causing interfacial reactions and perovskite degradation. Introduction of a rationally designed buffer layer or in-situ formed insulating layer *via* molecular reactions can suppress these harmful interfacial reactions in PeLEDs.^{7,8}
- Rational selection of EILs, HILs, and metal electrodes for PeLEDs. The electric field can accelerate the drift and diffusion motion of metal ions from

the metal electrode towards the perovskite emissive layer, leading to a detrimental influence on the device stability.^{9,10} Such issues can be resolved by the use of stable metals (e.g., Au) as well as excellent EIL and HIL with favorable interfacial properties and morphology stability under heat and electric fields.¹⁰ In addition, the hole-electron injection balance, and carrier confinement structure of the charge injection layer play a critical role in PeLEDs efficiency and operational stability.

- Enhancing the light out-coupling efficiency of the device. Since the estimated out-coupling efficiency of a PeLED is around 25 %, it is an effective way to further improve its EQE via special out-coupling designs.^{10,11} Besides, patterned ITO or metal electrodes with pre-designed micro-/nanostructures, effectively regulating perovskite with isolated platelets morphology, can improve the light extraction.

In the future, we should concentrate our study on obtaining a comprehensive understanding of both perovskite materials and devices. With systematic manipulations of compositions, additives, and underlying interface layers, PeLEDs with high efficiency and excellent operational stability will be possible. We anticipate that our primary studies included in this thesis would be insightful for future study of the PeLEDs.

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Part II

Scholarly Articles

Papers

The papers associated with this thesis have been removed for copyright reasons. For more details about these see:

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-179673>

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