Optoelectronic Devices Based on Perovskites/2D Materials

Heterostructures

Dissertation by

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ABSTRACT

Optoelectronic devices based on Perovskites/2D Materials

Heterostructures

This research explores the wide range of potential applications of perovskite heterostructures (PHSs). Recently, researchers have made considerable progress in optoelectronic devices based on PHSs for energy-related and sensing applications. Here we begin by introducing the fundamental theory of PHS and focus on its optoelectronic properties. We focus on fabricating and characterizing advanced semiconducting heterostructure optoelectronics devices. The main objective of understanding their fundamental behavior is to tailor and improve their functionalities and empower different applications. Therefore, we propose the development of light management in photo detectors using the following scalable and cost-effective fabrication techniques:

(i) The design of nano electronic and optoelectronic devices based on the layering of inorganic and organic hybrid Perovskite CH$_3$NH$_3$PbBr$_3$/Molybdenum disulfide MoS$_2$ single crystal. We developed a new method for stacking the n-type MoS$_2$ single crystal with p-type Perovskite CH$_3$NH$_3$PbBr$_3$ single crystal in the vertical direction, which enabled us to form a van der Waals heterojunction p–n diode. This demonstrates good current-voltage rectifying behavior in the dark and under light illumination.

(ii) The use of inkjet-printed photo detectors using Graphene/Perovskite/Graphene (GPG) Heterostructures in the visible light region. This is achieved by fabricating a graphene/perovskite metal-semiconductor-metal (MSM) configuration through inkjet printing or by employing the hybrid approach (a combination of inkjet printing and transferred layers) as a high-gain visible light photo detector.

This research opens a new path in the light management of optoelectronic devices.
Acknowledgement

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Chapter 1
Introduction

The field of PHSs has witnessed considerable progress in recent years due to the remarkably efficient photovoltaic and optoelectronic properties of these structures. This chapter reviews a wide range of potential applications of PHSs. The chapter begins by reviewing the fundamental theory of PHSs and pays special attention to their basic properties. The optical and electronic properties of PHSs are subsequently described in detail, with an emphasis on the approaches used to discover these properties. The crystal structures of heterostructures are examined by observing representative studies of the perovskite crystal. Recent scientific progress involving PHSs demonstrates the important role of optoelectronic properties of metamaterials, including those with PHSs.

Methylammonium lead trihalide, \( \text{CH}_3\text{NH}_3\text{PbX}_3 \) (\( X = \text{I}, \text{Cl}, \text{Br} \)), a crystalline material with a perovskite structure, is now one of the leading contenders for incorporation into contemporary photovoltaic technologies. In recent years, researchers have succeeded in significantly improving the power conversion efficiency (PCE) of this hybrid lead halide perovskite and have produced a record PCE, reaching up to 20.1%\(^1,2\) by using low-cost production methods. Accordingly, hybrid perovskites have been introduced into several photonic devices. One of the main considerations is the remarkable light-harvesting capabilities owing to the bandgap of \( \text{CH}_3\text{NH}_3\text{PbX}_3 \) being similar to the optimum for photovoltaic conversion, whereas the high extinction coefficient of the material ensures the effective absorption of light at a low mesoporous film thickness. However, to separate the excited state into charge carriers, there is a cost in terms of energy consumption for
both electron and hole injection. This is ultimately reflected in the degree of achievable efficiency.

The performance of semiconductor heterojunction devices has increased substantially since the introduction of heterostructures. PHS devices are fabricated by combining semiconductors of varying bandgap energies into a lattice of matching variables; these new structures now play an increasingly important role in optoelectronics. It has been observed that when heterogeneous materials are integrated into many electronic and photo-electronic devices, high-performance properties can be created. Evidence also suggests that some few-layered structures such as the transition-metal chalcogenides, which have 2D structures, exhibit good electronic and optical properties. The light absorption characteristics of the materials are significantly improved when multi-layered 2D materials are amalgamated with materials that are low-dimensional and single-layered (e.g. carbon nanotubes) or when integrated with PbS quantum dots. The concomitant improvement in their quantum efficiency (QE) enhances their activity in response to photo detection. [2]

Most current applications that use inorganic-organic perovskites (IOP) have high PCEs of up to 15% and large open-circuit voltages of up to 1.2 V. The majority of research indicates, however, that these devices do not exhibit good long-term stability and may have harmful qualities, including high toxicity. The most important optoelectronic heterostructures are solar cells, laser diodes, and photo detectors. The properties of IOPs are such that they can be used to develop low cost, hybrid PHSs with efficiencies...
exceeding 25%.[2-5] Our research focuses on discovering the material that optimizes energy stability and minimizes the variability of heterostructures. This objective led us to investigate the inorganic materials that may be combined with 3D organic perovskites, with the ultimate aim of studying the optoelectronic properties of the resulting PHSs. We also reviewed the tradeoffs resulting from engineering the structures of perovskites with organic cations capable of achieving the desired performance to raise the stability of the heterostructures, taking into account the optoelectronic properties of perovskite materials. One goal of this investigation is to overcome the toxicity concerns associated with lead-based perovskites.

Hybrid perovskite materials began to appear in photovoltaic materials in 2006. Miyasaka and colleagues used CH$_3$NH$_3$PbBr$_3$ as a dye-sensitized solar cell (DSSC) sensitizer. By using nanoporous TiO$_2$ in an electrolyte-based liquid, they achieved 2.2% efficiency. By replacing Br with I, the PCE$^{[2,6]}$ reached 3.8% efficiency. In 2011, Park and colleagues achieved 6.5% efficiency by implementing perovskite nanoparticles (~2.5 nm in diameter) on TiO$_2$ to reach an improvement in absorption of conventional dyes for sensitizers.$^{[7,2]}$

Snaith et al. describe the effect of replacing n-type TiO$_2$ electron transport material (ETM) with inert Al$_2$O$_3$; this replacement obtained a 10.9% efficiency.$^{[8,2]}$ Many researchers have noted the ambipolar nature of perovskites, and many have cited this as a major reason for the intensive growth in the use of planar heterojunction structures in devices.$^{[9-11]}$

In summary, hybrid perovskites offer an inexpensive way to achieve 20.1% PCE. This efficiency can be attained using well-known structures and preparation techniques. In this
chapter, we focus on recent developments in PSH fabrication and significant achievements resulting from the use of PHSs in photovoltaic applications such as the tendome cell and visible light communications. We also consider the current limitations of these materials with respect to their stability and their surface and interfacial defects.

1.1 Perovskite Heterostructures

1.1.1. Fabrication of Perovskite Heterostructures

Perovskite hybrids have been extensively fabricated and studied in recent years, notably in relation to their use in solar cells based on organic-inorganic lead halide perovskite. Perovskite hybrids have an excellent absorption from UV to NIR wavelengths, high carrier mobility, and large diffusion length of carriers comparable to silicon. The QE of perovskite has quintupled in the past five years from 4% in 2009 to its current level of near 20%. Perovskite materials are regularly incorporated in photovoltaic devices, mainly on the basis of their nanostructure form; hence, fundamental information about their crystalline structure and properties are not only important for perovskite-type crystal structure analysis but also for enhancing the utility of the material.
Perovskite materials are known to have a large optical bandgap. The bandgap of lead-based perovskites has approximately 1.5 eV and can achieve significant open-circuit voltages of more than 1.1 V. In previous works, researchers determined that the CH$_3$NH$_3$Pb$_{1-x}$Br$_x$$_3$ bandgap can be progressively adjusted from 1.6 to 2.3 eV by exchanging iodide with bromide. The disadvantages of perovskite materials currently in use are that they introduce stability and toxicity challenges that must be overcome before they can be used in devices. Thus, research into perovskites is facing an apparent decline. However, works focused on halide-based perovskite structures and properties have been published.$^{[2,13-17]}$

In this thesis, research pertaining to materials with the perovskite crystal structure and other ABX$_3$-type compounds, such as CH$_3$NH$_3$PbI$_3$, CH$_3$NH$_3$PbCl$_3$, and CH$_3$NH$_3$PbBr$_3$, are considered, and their performance as photovoltaic materials are compared. The structural lattice parameters of these three materials, which exhibit a perovskite
structure, are similar when compared with the cubic CH$_3$NH$_3$PbI$_3$, except for the lattice constants.$^{[17, 2]}$ The lattice parameters of these compounds are highly dependent on the size of the halogen ion, as shown in Figure1-2.

The p-n junction functionality, similar to a typical silicon solar cell, can be represented as silicon doped with a higher hole concentration (p-type) in contact with silicon doped with a higher electron concentration (n-type). The same would be the case with perovskite as a semiconductor which also has the functionality to dope. By contrast, the heterostructure design is comprised of an excellent absorbing material with long electron-hole diffusion lengths, and 2D transition-metal dichalcogenide materials (WS$_2$, MoS$_2$, graphene, and another inorganic compounds). For example, methylammonium lead halide perovskites (CH$_3$NH$_3$PbI$_3$) may control this restriction to some extent, by transferring the charge at the heterostructure interface such that it is not hampered by their band offsets.$^{[18]}$ Perovskites prepared from an excess of PbI$_2$, an excess of MAI, and stoichiometric amounts of precursors, exhibit identical film morphology but differ with respect to I–V hysteresis in a planar solar cell configuration.$^{[19]}$ To date, the poor stability of perovskite devices in air has limited sustained operation under normal conditions, and has consequently inspired researchers to address the issue of stability in future heterostructure developments to ensure long-term performance.

The defect energy distribution in the perovskite CH$_3$NH$_3$PbI$_3$ can be determined by employing the temperature-dependent admittance spectra. A comparison of perovskite-containing devices with transporting layer only devices confirms the presence of defect
response in the observed admittance spectra, which can be attributed to iodine interstitials.

The study of the defect reaction is an important consideration when characterizing the defect properties of a perovskite absorber and deepens the knowledge of the electronic structure of devices based on materials with a perovskite structure. For several point defects types, it could manifest in inorganic compounds and metal oxides.

Fundamentally, all types of defects could appear, but in general, some defects would be more prevalent. Although defect-dependent properties must be explored, it is important to examine the defect concentrations as a function of temperature in cases where the behavior of crystal components is familiar.

It is therefore necessary to devise reactions to introduce defects into materials. Defect formation may either happen internally in the solid or through interactions with the environment. Defect reaction rules can be designed and then applied to different defect structure systems. The point defects in a solid provide a good indication of where the point defects are dissolved in the solid solution. Concerning the chemical reactions and solutions thermodynamics, the defect equilibria may then be treated.
PHSs have recently been spotlighted because of their light-harvesting properties, low-trap densities for a solution-processed system, simple fabrication, energy, and high PCE. Although fabricating PHSs involve low production costs, large-scale manufacturing is often required. Most reported work focuses on solution processes to obtain thin-film heterostructures, mainly because these methods are cost-effective. Different absorbing layers and the top transparent electrode have been investigated with the ultimate aim of achieving high-performance devices.

Metal-halide perovskites are widely synthesized, largely because of their efficient use in optoelectronic applications. Many of the initial studies have controlled the optical and electronic properties of polycrystalline perovskite bulk films by reducing their size to a few nanometers to demonstrate quantum-size effects. The advantages of using
perovskites in optoelectronic devices include: (1) thinner layers for light harvesting, (2) efficient transfer of photo-induced charges to the heterointerface before recombination, and (3) low trapping losses.

Examples of materials with perovskite structures used in photovoltaic devices include MAPbI$_3$, MAPbBr$_3$, and MAPbI$_{3-x}$Cl$_x$, where MA is methylammonium. The energy levels of MAPbI$_3$ and MAPbI$_{3-x}$Cl$_x$ are approximately equivalent. As $x$ is small, most of the chlorine leaves the film in the form of methylammonium chloride (MACl) during perovskite formation.$^{[15]}$ The most significant advantage of lead halide perovskites is that it can be synthesized using inexpensive raw materials. These components usually consist of an organic compound and a lead salt. Methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) is synthesized by using organic compounds such as methylammonium iodide (MAI), and the lead salt is typically PbI$_2$ or PbCl$_2$.$^{[2,21]}

Figure 1-3. Synthesis and Assembly of Perovskite Heterostructures: Methods for Synthesizing Perovskite Thin Films: (a) one step (top) and two-step (bottom) SC, (b) Preparation steps using and architecture of (perovskite/MoS$_2$) (SC: Spincoating, TE: thermal evaporation).$^{[2]}$
Perovskite synthesis methods are depicted in Figure 1-3. The first technique is dual-source evaporation, in which the salt PbI₂ is co-evaporated on the substrate simultaneously to form the perovskite (Figure 1-3(a)). Another method is the spincoating process (Figure 1-3(b)) which is performed in the liquid phase in one step, using the same ingredients. The constituents then react during a thermal annealing process to form the perovskite. Another deposition method is to obtain the perovskite first, then submerge the lead salt film in the substrate, which is then exposed to MAI, which finally reacts with the salt to form the perovskite as shown in (Figure 1-3(c)).

It is now a common practice for researchers to combine materials with different properties to create layered heterostructures. This new method is useful for optoelectronics as it demonstrates new photo material properties and behavior according to its interfaces, lattice-matching, morphology, and other conditions. These conditions limit the quality of the aggregate material and interface that is achieved. This limitation can be avoided by using 2D vdW materials and metal oxide materials in the place of the PHSs.

Perovskite synthesis methods are shown in Figure 1-3. The first technique is dual-source evaporation in which the salt PbI₂ is co-evaporated on the substrate simultaneously to form perovskite (Figure1-3 a). Another method is the spincoating process (Figure 1-3 b) which is performed in the liquid phase in one step, using the same ingredients. The constituents subsequently react during a thermal annealing process to form perovskite. Another depositing method for perovskite involves dipping the lead salt film, which
exposes the substrate to MAI, leading to a reaction with the salt to form perovskite as shown in (Figure 1-3 c).

Researchers now combine materials with different properties to create layered heterostructures. This method is useful for optoelectronics as it demonstrates new photo material properties, displaying behavior via interfaces, lattice-matching, morphology, and other conditions. These conditions limit the aggregate material and interface quality that is achieved. This limitation can be avoided by using 2D vdW materials and metal oxide materials in place of the PHSs.

1.1.2 Device Architecture

Devices based on PHSs have led to significant advances in solar technology in the last few years, achieving (confirmed) PCEs of up to 20% in the laboratory, as shown in Figure 1-4. Perovskite device performance strongly depends on the device architecture which, in turn, dictates the choice of materials, the deposition methods for the material and naturally, the compatibility between the different components of the device. Progress in this area was achieved a few years into the research of photovoltaic materials and devices based on the perovskite CH$_3$NH$_3$PbI$_3$.

Perovskite devices consist of sandwich-like structures as shown in Figure 1-3. Two key representations of perovskite device architectures have planar and mesoscopic structures, while the inverted structure presents the hole transport layer (HTL) and electron transport layer (ETL). These devices are inversely positioned compared to
devices with a real perovskite structure.\textsuperscript{[24-26]} Mesoscopic structures have existed since the beginning of the evolution of perovskite solar devices. Perovskite can be defined as a thin layer that adequately covers the ETL in the absorber layer with charge transporting material.

The heterojunction can be described directly as a bilayer and bulk structure. In a bilayer device, an amount of charge is generated by carriers and depends on the exciton diffusion length, which is known to be in the range of 5-20 nm.\textsuperscript{[27]} Only photons absorbed via this heterojunction distance result in free charge carriers. All other excitons that are generated before reaching the donor and acceptor interface are lost to recombination and show very small power configuration efficiency.

For higher efficiencies, the heterojunction is distributed across the bulk of the device by mixing the acceptor and the donor materials. This consists of two interpenetrating networks: interconnected donor and acceptor domains; which represent a critical parameter that determines the device performance of the bulk heterojunctions. This parameter depends on the sizes of the donor and acceptor domains. The optimal domain size of exciton diffusion length is 10-20 nm.\textsuperscript{[2,28]}

Recent methodological improvements have included optimization of the perovskite solution and processing parameters to achieve advanced homogeneous films with a minor adjustment to the perovskite stoichiometry. This method permits tuning of the perovskite bandgap and absorption onset. The use of perovskites as optoelectronic materials has also advanced significantly in the last year. Perovskite devices based on
CH₃NH₃PbI₃ can be used as p-i-n heterojunction solar cells where the perovskite performs the role of intrinsic light absorber. The perovskite material mainly produces free carriers, which can have long carrier lifetimes of 300 ns and diffusion lengths exceeding 1 μm in polycrystalline thin films. Electron and hole transport properties were reported for CH₃NH₃PbI₃ and prepared by different synthetic methods.\(^{[29]}\)

A summary of reported PHSs accomplishments, including the materials and device structures is presented in Table 1 and Table 2. Most iodide-based perovskites achieve an open-circuit voltage up of 1 V with bromide-based perovskites reaching higher voltages because the bandgap is larger than that of the iodide. Organometallic perovskite materials can be used to obtain both p-i-n junction or p-n junction types because they have equivalent charge transport properties (Figure 1-4).

![Image](image_url)

*Figure 1-4. Progress in Power Conversion Efficiency of Silicon, Thin-Film, and Perovskite Devices.\(^{[2,33]}\)*
1.2 Applications

Researchers are actively collaborating to develop different solution processes and thin-film deposition techniques to enable them to obtain critical parameters to control the morphology and composition of hybrid perovskites. The development of PHSs has advanced our fundamental understanding of material chemistry for experimental and theoretical analysis. Rapid progress in the synthesis of perovskites and device fabrication has also facilitated the development of many optoelectronic applications including photodetectors, solar cells, light-emitting diodes, and lasers (Figure 1-5).
1.2.1 Photo detectors

The fabrication of high-performance photo detectors depends on using very thin films obtained via perovskite solution deposition. The first perovskite photo detector, which was reported by Yang,\cite{34} has a configuration similar to that of the standard perovskite solar cell. It operates at room temperature, has high detectivity, fast photoresponse, and performs similarly to conventional inorganic semiconductor photo detectors.\cite{34} Another group developed a technique that enabled the facile deposition of a perovskite film on a flexible ITO-coated substrate to obtain a flexible perovskite photo detector with high sensitivity and speed.\cite{35} Perovskite photo detectors have greater stability because they are not in direct contact with water; thus, their moisture sensitivity does not lead to degradation problems. Photo detector devices usually have bilayer heterojunction structures. This structure is convenient to fabricate and process, whereas the interfaces between bulk heterojunction architectures are smaller than those of perovskites and other functional materials. Photo detector devices typically contain bilayer heterojunction structures. These structures are convenient for fabricating and processing, while the interfaces between bulk heterojunction architectures are smaller than perovskites and other functional materials. Based on numerous studies, CH$_3$NH$_3$PbI$_3$/rGO,\cite{36} CH$_3$NH$_3$PbI$_3$/A10C60,\cite{37} and CH$_3$NH$_3$PbI$_3$/ PC61BM\cite{38} are bulk heterojunction structures that have also found application in photo detectors and solar cells (Figure 1-6).
Perovskite CH$_3$NH$_3$PbI$_3$ and graphene photo detectors exhibit a dramatically enhanced photo-responsivity of 1 A/W$^{-1}$ at 0.1 V.\cite{42} Efficient perovskite photo detectors are based on a perovskite polycrystalline thin film and are visible light photo detectors with high sensitivity, directivity, and stability. They use a CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ perovskite coating via a fluoride polymer.\cite{43} Moreover, the photo detector fabricated on the heterostructures is based on standard perovskites and 2D transition-metal dichalcogenides that have been fabricated and characterized. A photo detector based on heterostructure-based perovskites and 2D transition-metal dichalcogenides has been fabricated and characterized by many researchers. A thin layer of dispersive CH$_3$NH$_3$PbI$_3$ covered with WS$_2$ produces a photoconductor with a response of 17 A W$^{-1}$ and achieves high performance with an on/off ratio of $10^5$ owing to efficient interfacial charge transfer.\cite{2,39}

The integration of perovskites with semiconducting MoS$_2$ nanosheets, using solution
processing, has demonstrated high responsivity and a high on/off ratio.\textsuperscript{[44]} Mesostructured perovskite-based photo detectors are summarized in detail in Table 1.

\textit{Table 1-1. Summary of Reported Heterostructure Perovskite-Based Photo detectors Stability: \textsuperscript{a)}}

\textit{60 days with CYTOP protecting layer \textsuperscript{b)} air humidity < 15%}

<table>
<thead>
<tr>
<th>Device structure</th>
<th>( J_{sc} ) [mA/cm^2]</th>
<th>( V_{oc} ) [V]</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
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<tbody>
<tr>
<td>MAPbI\textsubscript{3}/PCBM \textsuperscript{50}</td>
<td>10.32</td>
<td>0.60</td>
<td>0.63</td>
<td>3.9</td>
</tr>
<tr>
<td>mp-TiO\textsubscript{2} /MAPbI\textsubscript{3} /spiro-MeOTAD \textsuperscript{57}</td>
<td>17.6</td>
<td>0.888</td>
<td>0.62</td>
<td>9.7</td>
</tr>
<tr>
<td>ZnO nanorod/MAPbI\textsubscript{3} /spiro-MeOTAD \textsuperscript{58}</td>
<td>16.98</td>
<td>1.02</td>
<td>0.51</td>
<td>8.9</td>
</tr>
<tr>
<td>mp-TiO\textsubscript{2} /MAPbI\textsubscript{3} /P3HT-MWNT \textsuperscript{59}</td>
<td>14.8</td>
<td>0.76</td>
<td>0.57</td>
<td>6.45</td>
</tr>
<tr>
<td>rutile TiO\textsubscript{2} nanorod/MAPbI\textsubscript{3} /spiro-MeOTAD \textsuperscript{60}</td>
<td>15.6</td>
<td>0.95</td>
<td>5.63</td>
<td>9.4</td>
</tr>
<tr>
<td>mp-ZrO\textsubscript{2} /MAPbI\textsubscript{3} /spiro-MeOTAD \textsuperscript{61}</td>
<td>17.3</td>
<td>1.07</td>
<td>0.59</td>
<td>10.8</td>
</tr>
<tr>
<td>ZnO nanorod/MAPbI\textsubscript{3} /spiro-MeOTAD \textsuperscript{62}</td>
<td>20.08</td>
<td>0.991</td>
<td>0.56</td>
<td>11.13</td>
</tr>
<tr>
<td>ITO/CdS/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/spiro-OMeTAD/Au \textsuperscript{63}</td>
<td>17.54</td>
<td>0.977</td>
<td>0.71</td>
<td>12.2</td>
</tr>
<tr>
<td>FTO/ZnO/MAPI/spiroOMeTAD/Ag \textsuperscript{64}</td>
<td>19.44</td>
<td>1.06</td>
<td>0.79</td>
<td>14.35</td>
</tr>
<tr>
<td>ITO/CuS/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/Cu/BCP/Ag \textsuperscript{65}</td>
<td>22.3</td>
<td>1.02</td>
<td>0.71</td>
<td>16.2</td>
</tr>
<tr>
<td>mp-TiO\textsubscript{2} /MAPbI\textsubscript{3} cuboid/spiro-MeOTAD \textsuperscript{66}</td>
<td>21.64</td>
<td>1.056</td>
<td>0.741</td>
<td>17.01</td>
</tr>
<tr>
<td>ZnO (25 nm)/MAPbI\textsubscript{3} /spiro-MeOTAD \textsuperscript{67}</td>
<td>20.4</td>
<td>1.03</td>
<td>0.749</td>
<td>15.7</td>
</tr>
<tr>
<td>polyTPD/MAPbI\textsubscript{3} /PCBM \textsuperscript{68}</td>
<td>16.12</td>
<td>1.05</td>
<td>0.67</td>
<td>12.04</td>
</tr>
</tbody>
</table>
Many studies have sought to develop solar cells based on the fabrication of PHSs. Perovskite solar cells can be divided into the following primary classes: 1) mesoporous active cells based on mesoporous TiO$_2$, 2) mesoporous passive cells based on mesoporous Al$_2$O$_3$, 3) planar-regular cells based on planar absorber layers with an ETL deposited on the transparent FTO/ITO, and 4) planar inverted cells based on an inverted layout where the HTL is deposited on FTO/ITO. Typical device layouts and their associated efficiencies are shown as solar cells based on a CH$_3$NH$_3$PbI$_3$/TiO$_2$ planar heterojunction (Figure 1-7).\cite{2,51-53} Utilizing perovskites as an absorber material in organic solar cells achieves the required solar to power conversion.\cite{6}
Mahaska et al. demonstrated the use of methylammonium lead halide perovskite\cite{6} as a light-harvesting material in organic solar cells. The PCEs of perovskite solar cells were found to be 3.81% for CH$_3$NH$_3$PbI$_3$ and 3.31% for the CH$_3$NH$_3$PbBr$_3$.\cite{6} Perovskite-based solar cells combine large carrier diffusion lengths coupled with good light absorption of solar cells and superior carrier transport properties when compared to regular inorganic thin-film solar cells. Park et al. fabricated solar cells using TiO$_2$ and CH$_3$NH$_3$PbI$_3$ with PCEs of up to 6.54%\cite{7}; however, these cells exhibited poor stability, and they degraded rapidly because of perovskite dissolution in the liquid. Snaith et al. increased the performance with an open-circuit voltage of more than 1.1 V by replacing TiO$_2$ with insulating mesoporous Al$_2$O$_3$. This replacement led to faster charge transport, and the photocurrent remained unaffected with higher PCE of 10.9%.\cite{9} A simple planar heterojunction solar cell, comprising perovskite (introduced by way of vapor deposition) as the light absorbing layer, was introduced by Snaith et al. and achieved PCE of 15%.\cite{8} The PCE of this solar cell
could reach 19.3% by improving the electron transport channel using Y-TiO₂, where Y is the ETL. Yang’s group fabricated a perovskite solar cell with high efficiency. They modified the ITO with poly(ethyleneimine) ethoxylate (PEIE) to decrease the ITO work function.⁵⁴ This two-dimensional material shows a strong ability to use compounds such as MoS₂ and graphene in a perovskite solar cell. Deng et al. demonstrated perovskite solar cells with stronger stability and a high PCE of 16.47%.⁴⁹,⁵⁵

Table 1-2. Summary of Reported Heterostructure Perovskite-Based Solar Cells

<table>
<thead>
<tr>
<th>Device structure</th>
<th>J_{sc} [mA/cm²]</th>
<th>V_{oc} [V]</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI₃/PCBM⁵⁰</td>
<td>10.32</td>
<td>0.60</td>
<td>0.63</td>
<td>3.9</td>
</tr>
<tr>
<td>mp-TiO₂/MAPbI₃/spiro-MeOTAD⁵⁷</td>
<td>17.6</td>
<td>0.888</td>
<td>0.62</td>
<td>9.7</td>
</tr>
<tr>
<td>ZnO nanorod/MAPbI₃/spiro-MeOTAD⁵⁶</td>
<td>16.98</td>
<td>1.02</td>
<td>0.51</td>
<td>8.9</td>
</tr>
<tr>
<td>mp-TiO₂/MAPbI₃/P3HT-MWNT⁵⁹</td>
<td>14.8</td>
<td>0.76</td>
<td>0.57</td>
<td>6.45</td>
</tr>
<tr>
<td>rutile TiO₂ nanorod/MAPbI₃/spiro-MeOTAD ⁶₀</td>
<td>15.6</td>
<td>0.95</td>
<td>5.063</td>
<td>9.4</td>
</tr>
<tr>
<td>mp-ZrO₂/MAPbI₃/spiro-MeOTAD ⁶¹</td>
<td>17.3</td>
<td>1.07</td>
<td>0.59</td>
<td>10.8</td>
</tr>
<tr>
<td>ZnO nanorod/MAPbI₃/spiro-MeOTAD ⁶²</td>
<td>20.08</td>
<td>0.991</td>
<td>0.56</td>
<td>11.13</td>
</tr>
<tr>
<td>ITO/Cds/CH₃NH₃PbI₃/Spiro-OMeTAD/Au ⁶₃</td>
<td>17.54</td>
<td>0.977</td>
<td>0.71</td>
<td>12.2</td>
</tr>
<tr>
<td>FTO/ZnO/MAPI/spiroOMeTAD/Ag ⁶₄</td>
<td>19.44</td>
<td>1.06</td>
<td>0.79</td>
<td>14.35</td>
</tr>
<tr>
<td>ITO/CuS/CH₃NH₃PbI₃/Car/BCP/Ag⁶⁵</td>
<td>22.3</td>
<td>1.02</td>
<td>0.71</td>
<td>16.2</td>
</tr>
<tr>
<td>mp-TiO₂/MAPbI₃ cuboid/spiro-MeOTAD ⁶⁶</td>
<td>21.64</td>
<td>1.056</td>
<td>0.741</td>
<td>17.01</td>
</tr>
</tbody>
</table>
Fundamentally, the operational principles of perovskite solar cells are similar to those of inorganic solar cells. The optical properties of the perovskite film result from an electron transfer to the TiO$_2$ and hole transfer. In this case, however, the optical processes are required to be kinetically fast compared to the recombination rates of photo-generated species and compared to the back-electron transfer rate of the interfaces between the TiO$_2$ or any material /hole transport layer/PHS.

1.2.3 LED and Lasers

Recent decades have witnessed slow progress in the field of perovskite light-emitting diode (LED) fabrications.[75] This is in contrast to the rapid development of solid techniques for fabricating organic LEDs (OLEDs). Organic-inorganic heterostructure electroluminescent (EL) devices have been fabricated using a combination consisting of the layered perovskite compound (C$_6$H$_5$C$_2$H$_4$NH$_3$)$_2$Pbl$_4$ (PAPI).
This LED has an emission peak at 520 nm at liquid-nitrogen temperature. Chondroudis and Mitzi fabricated a room temperature perovskite LED with a turn-over voltage of 4.8 V with approximately 0.11% efficiency. Miyasaka et al. report the development of MAPbI$_3$-based perovskite solar cells. The bright perovskite LED is composed of short-chain organic/inorganic hybrid lead halide perovskites and Friends et al. later demonstrated a sample. Perovskite LEDs have a turn-on voltage of 1.5 V and the perovskite layer coverage reviewed in this report remains low, which obviously lowers the device performance because of electrical shunts. Various deposition techniques were also developed to obtain high-quality perovskite layers. Most researchers presented an improvement efficiency because of the high-quality performance of perovskite LEDs.

As the modified structure improved, the QE decreases the nonradiative current losses. A recent example of an external QE achieved 1.2% efficiency. This study used organic poly (9,9-dioctylfluorene) to tune the bandgap of the charge-blocking layers. Friend et al. also report an LED with an impure blue color based on organic poly (9,9)-dioctylfluorene. They showed a color-pure perovskite LED with low turn-on voltages and higher luminance by using ZnO-based inorganic layers. Other researchers exploited the tunable bandgap and perovskites with different halide compositions to demonstrate that MAPbI$_{3-x}$Br$_x$ and MAPbBr$_{3-x}$Cl$_x$ (multi-colored LEDs) have different emissions ranging from near-UV to near-infrared. Most groups reported the deposition of perovskite absorber layers using a solution process. More recently, high-performance LEDs were developed with elevated QE and highly photoluminescent perovskite nanocrystals. Wang et al. reported perovskite LED performance which has the lower bandgap regions. This
generates electroluminescence which is confined by higher energy gaps of perovskite MQWs with high-efficiency radiative decay.\cite{85} Perovskites are also suitable candidates for semiconductor laser applications because of slow Auger recombination, large absorption coefficients, and low bulk defect densities. Zhu et al. demonstrated a solution-processed perovskite (MAPbX$_3$ where X = Cl, Br, I) film or single crystal perovskites at room temperature and wavelength-tunable lasering.\cite{86-87} Because of the broad stoichiometry-dependent tunability of the emission color, perovskites are promising materials for nanophotonics development, in parallel with the rapid development of perovskite photovoltaics. Ultra-stable amplified spontaneous emission was shown via perovskite lasers at strikingly low thresholds. However, the single crystal perovskite nanowire lasing threshold matches the charge carrier density as low as 1.5 × 10$^{16}$ cm$^3$ and estimated lasing quantum yields approaching 100% because of little charge carrier trapping.\cite{87} Moreover, single crystal perovskite solution processing with tunable broad emission multicolor perovskites is a promising material for nanophotonics.

1.2.4 Perovskite Tandem Integrated Devices

Designs based on tandem structures commonly consist of perovskite absorbers located between two cells. Calculations show that efficiencies exceeding 35% are possible\cite{88} with these perovskite on-perovskite tandem devices. The performance of the standard lead-based perovskite device has achieved the theoretical limit. The manufacturing advantages, i.e., simplicity and ease of integration, have been used in most research efforts in pursuit of a mechanically stacked tandem of perovskite devices to achieve stabilized efficiencies and long-term durability. The tandem structure design of both cells
is fabricated with perovskite active absorbers. The calculations of Hernán Míguez et al. demonstrated that perovskite on-perovskite tandem devices could achieve efficiencies of over 35%. The performance of standard lead-based perovskite devices is achieving the theoretical limit and considerable subsequent research has been devoted to investigating the optical and electrical properties of perovskite devices with the aim of developing devices with good efficiency and long-term durability. The efficiency of the single-junction domain in tandem devices mainly concerns the current distribution between two cells. There are many approaches to evaluating the potential efficiency of a tandem cell. For example, a tandem using a CH$_3$NH$_3$PbI$_3$-based top cell and a silicon heterojunction bottom cell could achieve efficiency of ~35-37%, based on light trapping.

1.2.5 Optoelectronic Devices Based on Perovskite for Visible Light Communications

Perovskite optoelectronic devices are developed for application in visible optical communications (VLCs). The replacement of radio-frequency wireless communication technologies by VLC has three advantages: open free bandwidth, secure data transmission, and environmentally friendly uses. Optical devices such as photo detectors and LEDs are suitable candidates for VLCs as they can simultaneously be used for lighting and data transmission. Furthermore, the emission of these devices can be modulated at high rates. However, in the VLC field, low-cost technologies are still needed to include white LED technologies that also experience a slow response time.\cite{89}
1.3 Future Challenges

Good progress has been made to solve the stability problem. Surface and interfacial defects have been recognized as the primary challenges for future research on perovskite devices.

1.3.1 Stability

The commercialization of lead halide PHSs has been challenging because of the toxicity of the Pb content and its high sensitivity to water. Moisture impacts the methylammonium lead iodide PHSs as these optoelectronic devices are soluble in water. Simulating exposure of the films to the rain effect and also dipping experiments demonstrated that, because of the balanced lead iodide solubility in water, with time, some amount of the Pb would dissolve. Han et al. reported that the carbon layer functions as a contact electrode, while this hydrophobic layer prevents moisture ingress and enhances the moisture stability of the device. Lately, many research studies have demonstrated lead-free perovskite materials together with commercialization such as Sn-based materials that have achieved an efficiency of 7%.

1.3.2 Surface and Interfacial Defects

The performance of PHSs is affected by the bulk properties of the absorber layer and the surface and interface between the absorber and carrier transport layers. In addition, the electrode contact layers are important for efficient carrier transportation. Recently, Burschka et al. improved the two-step methods for perovskite growth solution processes by developing vacuum deposition and vapor-assisted solution processing
methods. These methods enhanced the uniformity of interfaces and prevented direct contact between the hole and electron transportation layers.\[^{[11]}\] Further performance improvements in solar cells must account for at least three things. First, appropriate band alignments between the HTL and perovskites and between perovskites and the ETL is critical in order to make both the HTL and ETL suitable candidates for carrier transportation. Second, it is noteworthy that photo-excited electrons and holes are generated at the conduction band (CB) and valence band (VB) of a perovskite; thus, the electrons move to the CB of the ELT, whereas the holes move to the VB of the HTL. Large atomic sizes and loose crystal structures weaken the wrong bonds at the GBs, leading to essentially benign GBs in perovskites. Third, carrier transportation between different layers in PHSs are driven by the band-offset-induced electrostatic potential difference near the interfaces.\[^{[94]}\]

### 1.3.3 Surface Engineering

Efficient optoelectronic devices using a PHS have an additional degree of freedom to control recombination and charge transport. This would affect the balance relationship between the excitons and free charges to improve electron extraction in photovoltaic devices. Heterostructured materials with spatial carrier confinement could provide efficient luminescence because these materials allow the interplay between carrier mobility and the exciton binding energy to be controlled. This enables the design of new materials and optoelectronic devices with enhanced performance. Surface treatment is critical to creating a surface space charge region (Figure 1-8).
Many approaches to heterostructure surface treatment exist. The tuning of interface and interlayer properties is necessary to enhance the charge transport according to the type of defects that are generated as follows:

(1) **Plasma treatment**: Peng et al. found that generating S vacancies in MoS$_2$ through mild O$_2$ plasma treatment improves the hole transfer rate between CH$_3$NH$_3$PbI$_3$ / MoS$_2$. They highlighted the importance of defect engineering for tuning the band alignment of MoS$_2$ in heterostructures. Because of its isoelectronic nature, oxygen can passivate any S vacancy produced due to the exfoliation process. The electronic bandgap of MoS$_2$ show marked reductions by increasing the O concentration because of a notable change in the strength of Mo-S orbital hybridization at the edge of the VB.$^{[18, 95]}$ This method demonstrates the oxygen interaction with the MoS$_2$ monolayer as a useful way to achieve
air stability and excellent electronic properties of the dimensional material at the atomic scale.\textsuperscript{[95]} This treatment of the heterostructure is expected to exhibit maximum integrated intensity at the heterostructure interface due to defect-mediated recombination. Overall, this could lead to significant improvements in the characteristics of the diode behavior with a voltage-dependent photoresponse in the PHS.\textsuperscript{[96]}

(2) Chemical surface treatment: Surface chemical treatments make it possible to create a surface space charge region in the heterostructure. Chemical treatment of the n-type substrate creates an oxide layer on the sample surface. The layer could be removed and then the sample could be boiled in H\textsubscript{2}O\textsubscript{2} or water for approximately 15 minutes before rinsing the sample with deionized water. Alternatively, the sample could be submerged in KMnO\textsubscript{4} for a few minutes before washing it with deionized water.\textsuperscript{[97]} All of these treatments would create a stable depletion surface potential barrier. However, limited treatment is required for p-type substances. In the case of very low potential, etching in buffered HF followed by a water rinse is recommended.\textsuperscript{[98]}

(3) Using nanostructures and heterostructures of different n-type materials: Recent efforts have resulted in the fabrication of 2D materials and organic molecules with heterojunctions and heterostructures, such as a PHS, with diverse applications. The use of heterostructures or composite materials enhances the performance of 2D materials. Recently, there has been an effort to fabricate 2D materials and organic molecule heterojunctions and heterostructures, such as PHS, with potential diverse applications. The performance of 2D materials is enhanced through heterostructures or composite
materials. Composite materials with high HER activity\textsuperscript{99} and good supercapacitive performance\textsuperscript{100} are produced by integrating 2D materials with other materials that offer a highly available surface area and high conductivity, such as graphene. Recent work by Wu et al. resulted in the fabrication of a photoconductor with heterostructures of methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) perovskite films and WS$_2$ monolayers by using interfacial charge transfer and perovskite photoluminescence.\textsuperscript{39} Yan et al. reported phototransistors based on CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$/P3HT/graphene vertical multiheterojunctions with record responsivity of $\sim$4.3 $\times$ 10$^9$ A/W, several orders of magnitude higher than that of previous perovskite-based phototransistors.\textsuperscript{101}

\textbf{(4) Modification of the energy levels by the addition of interface layers:} Heterostructures are required to have good ohmic contacts on the interfaces between the absorber layer and contact electrodes for efficient charge transport. Considerable effort has focused on engineering various interfacial layers in a wide range of homojunctions. The interfacial layers consist of materials including inorganic metal oxides, polymer molecules, carbon materials, metal salts/complexes, organic-inorganic hybrids/composites, and other alternatives. Most of the interfacial materials have a direct impact on device efficiency and stability because of structural adjustments and property optimization of the interlayers. The interfacial modification in the electron-collecting electrodes is fundamentally the same as that of hole-collecting electrodes. Defect engineering is employed to tune the band alignment of MoS$_2$ in heterostructures as shown by Peng et al., such that ultrafast hole transfer from CH$_3$NH$_3$PbI$_3$ to MoS$_2$ would be possible with the CH$_3$NH$_3$PbI$_3$/MoS$_2$ interface by using mild plasma treatment.\textsuperscript{18}
interface physics of 2D transition-metal dichalcogenides (2D TMDCs) with halide perovskites is not well understood. Peng et al. discovered that mild O\textsubscript{2} plasma treatment creates S vacancies in MoS\textsubscript{2}, and it actively improves the hole transfer rate through the interface between CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/MoS\textsubscript{2}.\[^{18}\] Deng et al. reported a chemical modification of MoS\textsubscript{2} with a metal–organic compound (phenyl acetylene silver, PAS) as a clear example of chemical treatment through S atoms with transition-metal atoms.\[^{55}\] Most of the recent studies introduced a heterostructure containing MoS\textsubscript{2} in perovskite photovoltaic devices to enhance the hole transfer ability and extraction of the devices.\[^{55}\] Snaith et al. reported utilizing nanocomposites of graphene and TiO\textsubscript{2} nanoparticles as the electron collection layers in meso-superstructured perovskite solar cells, which showed promising photovoltaic performance with high PCE approaching 15.6%.\[^{102}\] Another possibility would be to employ rGS, which can be synthesized using a direct chemical procedure, as an interface layer for the fabrication of a perovskite solar cell. It was used as an interface layer between perovskite and TiO\textsubscript{2} films to ensure a large surface area and good conductivity to improve carrier transfer and the PCE of the solar cell up to 17.2%.\[^{103}\] Overall, much effort, including the promising use of thermal annealing and chemical treatments, has been devoted to control the defect and recombination processes.\[^{104}\]

PHSs uniquely combine the best optoelectronics properties that are required in heterostructure devices to obtain high-efficiency performance compared to other thin-film heterostructures. This chapter provided a comprehensive overview of fabrication methods and explored recent advances in applications of PHSs. Moreover, the relationship between engineering PHSs, its performance in applications, and future
challenges were also discussed. The stability and surface interface architecture of the layer under the perovskite film in different materials were also considered. We also evaluated the steps required to optimize the interface parameters, including the interfacial work function alignment with perovskite, which can improve the transfer of charges and increase the open-circuit voltage of the device. However, high charge extraction and transport capacities that optimize perovskite film growth are necessary for effective interfacial properties. Furthermore, material properties such as the ETL and HTL improve the device stability. The many advantages of PHSs, namely simple solution processing and tunable optoelectronic properties, suggest these materials have a promising future.

1.4 Objectives and Organization

Based on the above discussion, the main objectives of this work are enhancing the fabrication and characterization of the optoelectronics devices such as solar cells and photo detectors.

In chapter 3, perovskite CH$_3$NH$_3$PbBr$_3$ /molybdenum disulfide MoS$_2$ single crystal heterostructure was discussed. We found a new route to facilitate the design of nanoelectronic and optoelectronic devices based on layered inorganic and organic Perovskite CH$_3$NH$_3$PbBr$_3$ / Molybdenum disulfide MoS$_2$ single crystal. Stacking the n-type MoS$_2$ single crystal with p-type Perovskite CH$_3$NH$_3$PbBr$_3$ single crystal in the vertical direction enabled us to form a van der Waals heterojunction p–n diode which
demonstrates good current-voltage rectifying behavior in the dark and under light illumination.

In chapter 4, we introduced fully inkjet printing photo detectors MSM (2D materials & perovskite-based inks). We demonstrated the fully inkjet printing of 2D materials and perovskite for high-gain metal-semiconductor-metal (MSM) PD in the visible light region through the additive fabrication process of inkjet printing. Specifically, this work focused on the following: fabrication by graphene/perovskite MSM configuration by inkjet printing or by employing the hybrid approach (combination of inkjet printing and transferred layers) as a novel high-gain visible light photo detector; the formulation and characterization of nanoparticle-based conductive graphene inks and their in-depth characterization; and the designing and fabrication of fully inkjet printing MoS2/perovskite for visible light PD and its characterizations.
Chapter 2

Experiment and Methodology

In this chapter, we present the general experimental methodology used throughout the research. This includes in situ fabrication and characterization techniques to monitor thin film formation and ex situ measurements to characterize the heterostructure and properties of the thin films. PHS device fabrication and characterization were done to investigate the correlation between solution ink formulation, processing conditions, thin film structure and morphology, and PHS device performance.

2.1 In Situ Fabrication Techniques

2.1.1 Device Architectures and Sample Layout

For the investigations carried out in chapters 3 and 4, the device architecture was prepared as shown in Figure 2-1. The PHSs used in chapter 4 were prepared in the heterostructure architecture as shown in Figure 4-4. The active layer consists of the perovskite heterojunction formed by donor and acceptor as perovskite and 2 D material. For the PHS architecture, the holes are extracted through the Molybdenum disulfide or Graphene below the active layer and the electrons are extracted by the Perovskite on top as an active layer.

Finally, the electrodes on top and at the bottom are used for the lateral transportation of charge carriers. Since vastly different techniques are utilized for active layers, buffer layers and electrodes, which were sandwiched between the device and a thin glass cover in each section, the relative processing parameters will be presented in the related
sections. Since the inverted devices can avoid the use of air-sensitive electrodes, we did not encapsulate the inverted devices and directly characterized them in the air.

2.1.2 Focused Ion Beam Scanning Electron Microscopes (FIB-SEM)

An FIB setup is a scientific instrument that resembles a scanning electron microscope (SEM). However, while the SEM uses a focused beam of electrons to image the sample in the chamber, an FIB setup uses a focused beam of ions. The FIB can also be incorporated into a system with both electron and ion beam columns, allowing the same feature to be investigated using either of the beams. The FIB should not be confused with using a beam of focused ions for direct write lithography (such as in proton beam writing). These are generally quite different systems where the material is modified by other mechanisms.

2.1.3 Fabrication of Single CH$_3$NH$_3$PbBr$_3$ Perovskite /Mos$_2$ Heterojunction

Based on the description above, two different approaches were used for the device fabrication of Perovskite CH$_3$NH$_3$PbBr$_3$ / Molybdenum disulfide MoS$_2$ single crystal semiconductor nanostructures with different thicknesses and the fabrication of contacts for MoS$_2$-layer nanocrystals: (1) the FIB deposition method using platinum (Pt) as a contact metal described in Figure 3-2, (2) use of a shadow mask to deposit a gold (Au) contact. Figure 3-2 shows an image of the fabrication using the FIB to cut a thin crystal from the structure CH$_3$NH$_3$PbBr$_3$ perovskite single crystal device.
The fabrication process of the CH$_3$NH$_3$PbBr$_3$ /MoS$_2$ heterojunction is as follows. First, we mechanically exfoliated the MoS$_2$ thin flakes on the degenerately doped Si substrate covered with 285 nm thick SiO$_2$ using wet transfer method, as shown in Figure 3-2. The geometries and thickness of the thin flakes were identified using optical microscopy and atomic force microscopy, as shown in Figure 3-2. The MoS$_2$ with a thickness of approximately 3 nm and a relatively large lateral size was selected for the heterostructure fabrication. After locating the MoS$_2$ flakes under the microscope, electrodes were patterned using the shadow mask and FIB. The source electrode was conducted to the MoS$_2$ flakes while the drain electrode was conducted away from it (Figure 3-2). Finally, single perovskite crystals were picked up using the FIB and carefully positioned between the MoS$_2$ under the scanning electron microscope, as shown in Figure 3-2. The typical thickness of a CH$_3$NH$_3$PbBr$_3$ perovskite crystal is approximately 600 nm and was cut using the FIB-SEM. The heterojunctions were then formed between the overlapped region of MoS$_2$ and CH$_3$NH$_3$PbBr$_3$ perovskite. We designed the device by stacking the n-type MoS$_2$ single crystal with p-type Perovskite CH$_3$NH$_3$PbBr$_3$ single crystal
in a vertical direction. This enabled us to form a van der Waals heterojunction p–n diode. Devices studied in this research used gold as an electrode because of the higher stability of Au on perovskite during different measurements, which could very well demonstrate the concept of a vertical structure single crystal device.

2.1.4 Inkjet Printer

The DMP-2831 allows the deposition of fluidic materials on an 8 x 11 inch or A4 substrate, utilizing a disposable piezo inkjet cartridge. This printer can create and define patterns over an area of about 200 x 300 mm and handle substrates of up to 25 mm thick with an adjustable Z height. The temperature of the vacuum platen, which secures the substrate in place, can be adjusted up to 60°C. Additionally, a waveform editor and a drop-watch camera system allow manipulation of the electronic pulses to the piezo jetting device for optimization of the drop characteristics as it is ejected from the nozzle. This system enables easy printing of structures and samples for process verification and prototype creation. To minimize waste of expensive fluids, each cartridge reservoir has a capacity of 1.5 ml. The cartridges can easily be replaced to facilitate printing of a series of fluids. Each single-use cartridge has 16 nozzles linearly spaced at 254 microns with typical drop sizes of 1 and 10 picoliters.

2.1.5 Fabrication of All Inkjet Printed Graphene/CH₃NH₃PbClₓIₙ Perovskite/Graphene Heterostructures

Inkjet printing will print the interdigital electrodes using a DMP-2800 printer. First, the substrate is cut into required sizes and cleaned with acetone, isopropyl alcohol and
distilled water, and then dried with flowing nitrogen. We employed various types of substrates such as PET, FTO, flexible PEN, glass and ITO.

Figure 2-2. Two types of Photodetector Metal–Semiconductor–Metal (MSM) and Graphene–Semiconductor–Graphene (GSG).

Then, the contact electrodes are deposited on a square pad featuring different gaps (150 µm, 200 µm, 250 µm), and an interdigitated electrode design as demonstrated using Advanced Design System (ADS) Software (Figure 2-3). For the MSM photodetector, Au and Ag can be deposited by both thermal evaporations with a shadow mask or by inkjet printing, enabling us to compare the results. In the case of the graphene–semiconductor–graphene (GSG), the electrodes used an inkjet printer with the same geometrical characteristics. Finally, the photoactive layer was deposited by inkjet printing to completely cover the gap between the two electrodes to avoid short-circuiting. The active area was covered with two types of perovskites (\(\text{CH}_3\text{NH}_3\text{PbCl}_x\text{I}_{3-x}\), \(\text{CH}_3\text{NH}_3\text{PbI}_3\)).
2.1.5.1 Ink Formulation

To obtain the best results for exfoliation of graphene and other 2D materials, we adopted some of the well-understood methods for the ink formulations. A mixture of graphite in DMF solvent was sonicated for a given period. The resultant suspension was centrifuged to obtain thick flakes in the sediment and the supernatant was harvested and added to the ethyl cellulose. Terpineol was added to the graphene/DMF solution for solvent exchange. DMF was exchanged with terpineol using a rotary evaporator with a vacuum distillation technique. After boiling off the DMF, the remaining graphene ink was harvested separately. To check the graphene concentration, a small volume of ink solution was diluted with terpineol for optical absorbance studies. For printing, the graphene ink was mixed with ethanol to optimize the viscosity for inkjet printing.

2.2 Ex Situ Characterization Techniques

2.2.1 Film Thickness Measurement

The thickness of thin films was measured using a profilometer (Tencor). A profilometer scans a surface with a small needle and registers height differences. The lateral resolution
was in the μm range due to the diameter of the tip of the needle, but the height resolution was in the nm range. The thickness of a film was measured by removing a part of the film via scratching and measuring the difference from the surface of the film to the bottom of the gap.

2.2.2 Atomic Force Microscopy (AFM)

In this research, AFM was used to study the surface morphology and roughness of thin films. AFM experiments were performed using a dimension ICON SPM system, (Bruker, USA). Commercial silicon tips with a nominal spring constant of 40 N/m and resonant frequency of 300 kHz were used in all the experiments. Atomic force microscopy measurements were performed to investigate the surface topography of the thin films and to calculate their surface roughness. Phase imaging by AFM revealed information about the size and shape of the existing phases on the top surface.

2.2.3 X-Ray Diffraction Measurements

Single-crystal X-ray diffraction measurements were executed on a Bruker SMART APEX-II diffractometer equipped with a CCD detector (graphite-monochromated Mo-Kα radiation, \(\lambda = 0.71073 \, \text{ Å}\)) at room temperature. Data integration and refinements were carried out with APEX2 software. X-Ray powder diffraction (XRD) of polycrystalline material taken from the reaction solution was also collected using a Bruker-AXS D8 ADVANCE X-Ray diffractometer with Cu-Kα1 radiation (\(\lambda = 1.54186 \, \text{ Å}\)) in the range of 10°-90° (2θ) with a time setting of 0.1 seconds per step and a step length of 0.002°. During the experiment, samples were kept in an N₂ box.
2.2.4 Transmission Electron Microscopy (TEM)

TEM microscopy images were acquired using a transmission electron microscope (Titan Cryo Twin, FEI Company, Hillsboro, OR) with a 4k x 4k charged couple device (CCD) camera (model US4000) and an energy filter (model GIF Tridiem from Gatan), Inc. (Gatan Inc., Pleasanton, CA). The GIF was utilized in energy-filtered TEM (EF-TEM) mode to image the Carbon and Sulfur distribution in the sample. The carbon edge located at 284 eV and Sulfur edge at 165 eV were selected to generate the EF-TEM maps using a 3-window method. The samples were prepared by floating the active layer and transferring them onto a copper (400 mesh) grid. The analysis was carried out using an FEI Titan ST TEM working at 300 keV. Low-intermediate imaging and high-resolution TEM (HRTEM) characterizations were performed to investigate all the samples at room temperature.

2.3 Device Performance

2.3.1 Electrical characterization

All the electrical parameters of the devices were measured with a semiconductor characterization system (Keithley, Model SCS-4200) assisted by a probe station. Monochromatic light was obtained with a xenon lamp at a wavelength of 630 nm, and a power meter was used to measure the light intensity. Electrical characterization of the photo detectors was described with and without light illumination using a semiconductor parameter analyzer. Wavelength-dependent electrical properties can also be determined using a broadband light emitting source, such as a Xe lamp.
2.3.1.1 Current Density-Voltage Characteristics

The current density-voltage characteristics of the PHS were measured using a Keithley 2400 under a simulated AM 1.5G solar irradiation at 100 mW cm$^{-2}$. Solar simulator irradiance was calibrated using a standard silicon photovoltaic with a KG1 filter calibrated by the National Renewable Energy Laboratory. To measure external quantum efficiency (EQE) spectra, the fabricated devices were illuminated by monochromatic light and the generated current was recorded as a function of the wavelength of the light. The EQE spectra were generated by calibrating the device current with a current generated by a photodiode with a known EQE. The EQE measurements were performed using an Oriel Quantum Efficiency Measurement Kit (Newport).
Chapter 3

Perovskite CH$_3$NH$_3$PbX$_3$/Molybdenum Disulfide MoS$_2$ Single Crystal Heterostructure

Perovskite CH$_3$NH$_3$PbX$_3$ is a crystalline material that can effectively be incorporated in perovskite heterostructure due to its efficient photovoltaic properties. In recent years, the PCE of perovskite CH$_3$NH$_3$PbX$_3$ has significantly improved making the material one of the leading rivals to contemporary photovoltaic technologies. Unlimited development of the hybrid lead halide perovskite CH$_3$NH$_3$PbX$_3$ (X = I, Cl, Br) has produced a record PCE, reaching up to 20.1% [109] using low-cost production methods. Accordingly, hybrid perovskites have been introduced into several photonic devices, finding a promising application in photovoltaic technology. One of the main considerations is the light absorption because the CH$_3$NH$_3$PbX$_3$ bandgap is close to the optimum for photovoltaic conversion, while the high extinction coefficient of the material ensures a good absorption of the light at a low mesoporous film thickness. However, in order to separate the excited state into charge carriers, an energy price has to be paid for both electron and hole injection directly reflected in the achievable efficiency. The performance of semiconductor heterojunctions has markedly increased since the introduction of heterostructures. PHSs devices are created by combining semiconductors of varying bandgap energies into a lattice of matching variables; these new structures are playing an increasingly important role in optoelectronics. It has been observed that when heterogeneous materials are integrated, many electronic and photo-electronic devices with high-performance properties can be created. It has been established that some few-
layered structures like the transition-metal chalcogenides, which are 2D materials, have good electronic and optical properties. When such multi-layered 2D materials are amalgamated with materials that are low dimensional and single-layered, such as carbon nanotubes, or when integrated with the PbS quantum dots, the light absorption of the materials is highly improved, and their QE is also improved, and thus they become quite active in response to photo detection. \[110\]

Most of the current applications that use IOPs have high power conversion efficiencies of up to 15% and large open-circuit voltages of up to 1.2 V. Most of the research indicates, however, that these devices are not stable over time and may display harmful qualities such as toxicity. The most important optoelectronic heterostructures are solar cells, laser diodes and photo detectors. The properties of IOPs can be used to develop low cost, hybrid perovskite heterostructures with efficiencies above 25\%.[1-3] To determine the best material that optimizes energy stability and minimizes variability of heterostructures, we paid special attention to inorganic materials that combine with 3D organic perovskites to study the effect of optoelectronic properties on the resulting perovskite heterostructures. We also reviewed the tradeoffs that result from engineering perovskites with performance organic cations to raise stability of the heterostructures while characterizing the optoelectronic properties of perovskite materials to avoid the toxicity concerns of the lead-based perovskites.

In 2006, hybrid perovskite materials began to appear in photovoltaics. Miyasaka et al. \[111\] used CH$_3$NH$_3$PbBr$_3$ as a DSSC sensitizer. By using nanoporous TiO$_2$ in an electrolyte-based liquid, they achieved 2.2% efficiency. By replacing Br with I, the power conversion
efficiency (PCE) reached 3.8%.\textsuperscript{[112]} Park et al. achieved 6.5% efficiency by implementing perovskite nanoparticles (\( \sim 2.5 \) nm in diameter) on TiO\(_2\) to achieve an improvement in absorption of conventional dyes for sensitizers in 2011.\textsuperscript{[113]} Snaith et al. described the effect of replacing n-type TiO\(_2\) ETM with an inert Al\(_2\)O\(_3\); this replacement achieved a 10.9% efficiency.\textsuperscript{[109]} Many reports have noted the ambipolar nature of perovskites, and many have cited this nature as a major reason for the intensive growth in the use of planar heterojunction structures in these devices.\textsuperscript{[114-118]}

In this project, we will create a new design of nanoelectronic and optoelectronic devices based on layered inorganic and organic Perovskite CH\(_3\)NH\(_3\)PbBr\(_3\)/ Molybdenum disulfide MoS\(_2\) single crystal. Stacking the n-type MoS\(_2\) single crystal with the p-type Perovskite CH\(_3\)NH\(_3\)PbBr\(_3\) single crystal in the vertical direction enables us to form a van der Waals heterojunction p–n diode. Also, we showed good rectifying behavior using a single crystal device via developments in PHS fabrication and significant achievements using perovskites heterostructures in photovoltaic applications such as tendome cell and visible light communications.

### 3.1 Research Motivation

Perovskite CH\(_3\)NH\(_3\)PbBr\(_3\) is a crystalline material that can effectively be incorporated in solar cells due to their efficient photovoltaic properties. In recent years, the PCE of perovskite CH\(_3\)NH\(_3\)PbBr\(_3\) has significantly improved, which has promoted the material to one of the leading rivals to the contemporary photovoltaic technologies. It is established that the compound 2D MoS\(_2\) has very strong electronic properties with good qualities as
a charge carrier. The metallic structure of the compound has high semiconducting abilities or response with equal high on/off ratios.\textsuperscript{[4]} Structurally, the heterostructure of the Perovskite CH\textsubscript{3}NH\textsubscript{3}PbBr\textsubscript{3}/Molybdenum disulfide MoS\textsubscript{2} single crystal is characterized by a chemically exfoliated 2D MoS\textsubscript{2} and perovskite into monolayer nanosheets. The resultant structure is a planar heterojunction photovoltaic cell that contains vapor deposited perovskite that acts as the absorbing layer with up to 20% solar-electric PCE. This is particularly attributed to the electronic properties of the 2D Molybdenum disulfide MoS\textsubscript{2} single crystal which has a significantly high responsivity as well as the high on/off ratios of the semiconducting phase. It has been observed that when heterogeneous materials are integrated, many electronic and photo-electronic devices with high-performance properties can be created. It has been established that some few-layered structures like the transition-metal chalcogenides, which are 2D, harbor good electronic and optical properties. When such multi-layered 2D materials are amalgamated with materials that are low-dimensional and single-layered materials such as carbon nanotubes, or when integrated with the PbS quantum dots, the light absorption of the materials is highly improved, and their QE is also improved, and thus they become quite active in response to photo detection.\textsuperscript{[119]} It has also been established that when then the 3D components or the molecular layers of amorphous silicon and the fluorescent dye of rhodamine 6G are integrated with organolead trihalide perovskites, they have the ability to make modifications to the light interaction of the 2D materials. It is true that the 2D TMDs which are the organolead trihalide perovskites with the compound formula of MAPbX\textsubscript{3} have desirable properties like free carrier diffusion lengths for longer durations and thus have
high absorption qualities.$^{[5]}$ They have high performance when used in the production of solar cells. It is, therefore, imperative that to develop effective photo detecting devices, the integration of multi-layered compounds such as lead halide perovskites having 2D TMDs and the one walled structure should be considered as the integrated compound, as it has charge transfer levels for light interactions for photo detection. Perovskites can, therefore, be used as absorption layers via integration with graphene. Typically, the graphene oxide layer which has been reduced, that is, MoS$_2$, WS$_2$, and WSe$_2$. Has demonstrated improvement in photo-responsivity when used in the production of photo detectors. A challenge, however, arises when improving photo-responsivity when the dark state current is low. This challenge is often associated with 2D material photo detectors which have been made from the integration of the perovskites. The challenge is common with layers of the graphene because they are highly conductive 2D materials and do have substantial current when in the dark off-state, so during the photo state the current becomes low. Hence, it becomes difficult to achieve the overall consistent on/off ratio. It has been found that to create high photo detection responsivity, the 2D layers should be deposited by mechanical exfoliation or by the use of chemical vapor deposition.$^{[120]}$ Many integrated devices which have large areas can easily be tested during their fabrication when the solution depositions used are also large area and have high-quality chemical exfoliation of the 2D materials. The solution-processed heterostructure is fabricated from the 2D MoS$_2$ amalgamated with the perovskite which has proved to be effective in photo detection. To fabricate the structure, much MoS$_2$ powder which is chemically exfoliated should be used. The method needed to obtain viable results is
lithium intercalation which uses monolayer nanosheets that are soluble in water. To obtain a pure concentration of the metallic phases and the semiconducting phases, fabrication of the nano sheets should be characterized using Raman and x-ray spectroscopies of photoelectricity (XPS)\[6\]. To obtain MoS\(_2\) nano sheet depositions that are uniform, the process should be conducted using vacuum filtration and thus MoS\(_2\) is transferred to the target substrate. 2D MoS\(_2\) normally exhibits two forms depending on its semi conduction phase. They are trigonal prismatic which is the 2H phase, and metallic octahedral which is the 1T phase. When bulk MoS\(_2\) is chemically exfoliated via lithium intercalation, the nano sheets obtained are primarily 1T phase and are thus electrically conductive. The phase is metastable, and thus the stable phase of 2H-MoS\(_2\) is achieved thermodynamically in a vacuum through the process of annealing at 300\(^{\circ}\)C or in argon gas for 2H. The concentration of the 1T phase is approximately 70\% at room temperature but is at 0\% when it undergoes an annealing process at 300\(^{\circ}\)C. For the 2H phase, the concentration is 100\% after annealing.\[121\]

The thickness of the MoS\(_2\) and the corresponding phase of the nano sheet contributes considerably to the performance of the photo detectors. That is why it is significant that the thickness of the solution be controlled during vacuum filtration. The thickness of the nano sheet film resonates with an electrically percolating layer at almost 80\% channel surface coverage, but not with a thick film which is multi-layered.

In recent years, hybrid perovskite devices have been able to combine the advantages of both organic and inorganic components. They have been largely used in optoelectronic applications, for instance, in solar cells, photo detection, and light-
emitting devices, among others. The materials made of a 2D member of perovskite have a generic formula of RNH$_2$PbX$_4$ where X is a halide and R is an alkyl.$^{[122]}$ A thin-layered crystal of perovskite, particularly (C$_4$H$_9$NH$_3$)$_2$PbBr$_4$, displays efficient photoluminescence (PL) as was effectively synthesized by the Yang group. The inorganic component (Pb) gives the photo detector opportunity for a wide bandgap range and increased carrier mobility. The photo detectors made of perovskite/graphene have rich optical properties, a high absorption rate, and an enhanced carrier diffusion rate.$^{[123]}$ In this regard, the improved electrical and optical properties offer an opportunity to develop new solutions to solve issues in optoelectronic devices. Nevertheless, due to unstable 2D perovskite in solvents such as water or acetone during the microfabrication process, success has never been realized when integrating 2D and perovskite into a particular functional nano-scale.

3.2 Results and Discussion

Here, the p–n junctions were investigated using organic perovskite CH$_3$NH$_3$PbBr$_3$ single crystal and 2D MoS$_2$ as the p- and n-type semiconducting materials respectively. Current-rectifying behavior was clearly observed in the junction device. The rectification ratio could be electrically tuned by the thickness of the 2D nature of the heterostructure. The devices also showed good photo response.

The fabrication process of the CH$_3$NH$_3$PbBr$_3$ perovskite/MoS$_2$ heterojunction is as follows. First, we mechanically exfoliated the MoS$_2$ thin flakes on the degenerately doped Si substrate covered with 285 nm thick SiO$_2$ using the wet transfer method as shown in
Figure 3-1. The geometries and thickness of the thin flakes were identified using optical microscopy and atomic force microscopy as shown in Figure 3-1. The MoS2 with a thickness of about 3 nm and a relatively large lateral size was selected for the heterostructure fabrication. After locating the MoS2 flakes under the microscope, electrodes were patterned using the shadow mask and FIB. The source electrode was conducted to MoS2 flakes while the drain electrode was destined from it (Figure 3-2).

Finally, single perovskite crystals were picked up using FIB and carefully positioned between the MoS2 under a scanning electron microscope as shown in Figure 3-2. The typical thickness of CH₃NH₃PbBr₃ perovskite crystal was around 600 nm and was cut using FIB-SEM. The heterojunctions were formed between the overlapped region of MoS2 and perovskite. We predeceased the device by stacking the n-type MoS2 single crystal with p-type perovskite CH₃NH₃PbBr₃ single crystal via the vertical direction. This enabled us to form a van der Waals heterojunction p–n diode. Devices studied in this research use gold as electrodes due to the higher stability of Au on perovskite with different measurements,
which could successfully demonstrate the concept of a vertical structure single crystal device.

Figure 3-2. (a,b,c) fabrication using the focused ion beam (FIB) to cut thin crystal from the structure CH$_3$NH$_3$PbBr$_3$ (d) CH$_3$NH$_3$PbBr$_3$ perovskite single crystal on top of molybdenum sulfide (MoS$_2$) monolayer semiconductor nanostructures with 600nm thicknesses.
Based on the description above, we had two different approaches for the device fabrication of perovskite CH3NH3PbBr3 / Molybdenum disulfide MoS2 single crystal semiconductor nanostructures with different thicknesses. The fabrication of contacts for MoS2-layer nanocrystals was performed in two steps: (1) the FIB deposition method using platinum (Pt) as a contact metal as described in Figure 2, and (2) using a shadow mask to deposit a gold (Au) contact. Figure 3-2 shows an image of the fabrication using the FIB to cut a thin crystal from the structure CH3NH3PbBr3 perovskite single crystal device.

Figure 3-3 Thickness of CH3NH3PbBr3 Perovskite.

Figure 3-3 shows CH3NH3PbBr3 perovskite single crystal on top of molybdenum sulfide (MoS2) monolayer semiconductor nanostructure with 600 nm thickness.
Figure 3-4. The absorption spectrum of a) MoS$_2$ and b) CH$_3$NH$_3$PbBr$_3$ Perovskite.

UV–Vis absorption spectra of CH$_3$NH$_3$PbBr$_3$ perovskite/ MoS$_2$ molybdenum sulfide vdW solids prepared were recorded on SHIMADZU UV-3101PC UV–vis-NIR scanning spectrophotometer. The spectra is caused by the low bandgap absorption which only becomes significant in very thick single crystals. Figure 3-4 shows the MoS$_2$ structure spectra. The crystal has an interlayer van der Waals interaction and hexagonal in-plane
structure. A single crystal structure of perovskite corresponds to a projection on the ab plane. The absorption spectrum of MoS$_2$ and perovskite in Figure 3-4 shows the band gap alignment of our PHS. It clearly confirms that the Type I heterojunction straddling the bandgap of one semiconductor is completely contained in the bandgap of the other one. The discontinuities of the bands are such that both types of carriers, electrons and holes, need energy to change from the material with the smaller bandgap to the one with the larger gap. The carriers from the other side gain this energy.

![Current-Voltage Characteristics](image)

*Figure 3-5. Typical I-V characteristics of Perovskite Single Crystal / MoS$_2$ p-n heterojunction device*

Electrical transport characterizations of the heterojunction p–n diode were performed as shown in Figure 3-5. The device shows standard p–n diode characteristics with clear rectifying behavior, with the current being able to pass through the device only when the p-type perovskite is positively biased. The strong current-rectifying characteristic
indicates that a good van der Waals p–n heterojunction was formed between n-type layered MoS$_2$ and p-type perovskite thin semiconductors. MoS$_2$ and perovskite single crystal create good optical properties such as large excitonic absorption and PL, which illuminated light on a high-performance p–n junction for optoelectronic applications. When the excitation photon energy is larger than the bandgap of MoS$_2$ and perovskite single crystal, electrons will be excited from the VB to the CB, which will generate the photocurrent.

To evaluate the performance, we used a 405 nm semiconductor laser, which can excite the carriers both in MoS$_2$ and perovskite as the illumination source to investigate the photo response properties of the heterostructure.

3.3 Conclusion

Perovskite / MoS$_2$ single crystal is a research area that is very interesting for semiconductor optoelectronics. We conducted an investigation into an organic single crystal and a 2D MoS$_2$ single crystal as the p- and n-type semiconducting materials which resulted in a p-n junction. The current rectification behavior of the typical p-n junction can be clearly seen on the device. We summarized the origins of the optical and electronic properties using the perovskite crystal structure as heterostructures. The 2D heterostructure nature allowed us to change the rectification ratio electrically by tuning the gate voltage. This device also demonstrates photo response properties and fast response time. These results suggest a new direction to aid in the design of nano-optoelectronic devices based on layered inorganics and organics.
Chapter 4

Fully Inkjet-Printed Photo Detector using a
Graphene/Perovskite/Graphene (GPG) Heterostructure

The markets for optoelectronic devices including photo detectors (PD)\textsuperscript{[124]} and photovoltaics (PV)\textsuperscript{[7]} have expanded rapidly in the past two decades due to intense research and development driven by technological necessity.\textsuperscript{[125-130]} In principle, PD converts the incident photons into electrical signals that are attractive in various applications such as optical communications and surveillance and chemical/biological sensing. Various semiconducting material systems and device configurations have been explored in the literature with high responsivity and low detection limits. Most commercial PDs are comprised of Si due to the industrial advancement and maturity, it has demonstrated over the years. However, solution processable PDs with their ease of fabrication, low power consumption, fast response time, broadband detection and a large detectivity are quite manageable.

Over the past few years, low-cost solution-processed monolayer/few-layered 2D materials (such as graphene, MoS\textsubscript{2} and MoSe\textsubscript{2}) and hybrid perovskites have attracted considerable attention for various applications including solar cells, LEDs, phototransistors, and lasers. Hybrid perovskites are especially attractive in solar cells due to their excellent photoelectric properties including a high absorption coefficient, extended diffusion length, and high QE in the solar region. The heterojunction of mono/few-layered 2D materials with hybrid perovskites are perfect candidates for
low cost, high efficient optoelectronic devices which combine the advantages of excellent light absorption and electronic transportation characteristics. Printed electronics is an emerging field that is expected to revolutionize the manufacturing industry with low cost electronic devices. Printed devices have the advantages of being able to be deposited on a wide range of substrates over large areas at relatively low/room temperatures. Moreover, inkjet printing is a non-contact process capable of precise fabrication on a substrate with predetermined patterns. Any material can be deposited in the inkjet printing technique if it can be dispersed in a solution. Examples of functional materials which have been inkjet-printed include semiconductors and polymers, fullerene mixtures, quantum dots, metal nanoparticles and carbon nanotubes. The fabricated devices range from transistors, LEDs, solar cells, supercapacitors, and sensors. [131-132]

This project aims to produce graphene and other 2D material ink formulations suitable for inkjet printing. Organic-inorganic hybrid 2D perovskites have shown promising PV characteristics, but have been proven to be difficult materials to fabricate with vapor deposition methods. Hence, we will focus on developing perovskite inks suitable for inkjet printing. The project objectives are fabricating flexible devices based on 2D materials /perovskites using low-cost, scalable material production and device fabrication. The main goal is to achieve a graphene/perovskite-based ink as a heterostructure as it will be a promising direction in graphene electronics. Heterostructure fabrication by 2D printing or by using the hybrid approach as a combination of printed and transferred layers is a new stage of development in
graphene/perovskite-based heterostructures and 2D material printing electronics. High stability in the ambient environment is a result of inorganic nanoparticles (NPs) as optoelectronic materials.\textsuperscript{133} The produced inks will be characterized by various techniques for optical, electrical and optoelectronic properties in order to achieve high-quality printing of devices on flexible substrates such as polyamide. Graphene/perovskite inkjet printing is a low cost and multipurpose technique of deposition to produce conductive and transparent thin films. Here, we will use two types of graphene inks, an ink prepared by graphite intercalation with the surfactant, and pure graphene exfoliated from top-down dispersion in an exchange polymer.

Functionalization of graphene during intercalation can optimize the donor-type where it can be viewed as a macro carbanion. Functionalization increases the need to apply a bulk graphite precursor to achieve better conductivity. The two inks are immediately inkjet printable with good jet spreading.\textsuperscript{134} However, the sheet resistance of the deposited films will vary with different printing passes for both ink types, due to the larger graphene sheet size in the ink which reduces the number of sheet-to-sheet contacts along the conductive way.\textsuperscript{134}

This project will focus on advancements of inkjet printing-based fabrication regarding active deposition and electrode deposition for optoelectronic devices, such as photo detectors, photovoltaics, and transparent electrodes. The inkjet printing techniques can overcome the challenges existing in traditional fabrication processes and can therefore produce new functionalities and improve the performance of the existing processes. We present 2D material/perovskite heterojunctions as having great
potential for a wide spectrum of applications in optoelectronics. We propose fully inkjet printing MSM photo detectors and an electrode fabrication process by inkjet printing.

4.1 Research Motivation

The 2D layered inkjet printing photo detectors with hybrid perovskite represented asRNH$_2$PbX$_4$, where X is halide and R is alkyl, are presently synthesized because they are likely to exhibit rich optical characteristics such as exciton and fluorescence effects [11, 12]. Few studies, however, have reported on optoelectronic measurements and the transport of individual 2D perovskite crystals. This, therefore, may be the reason for the challenges of instability during fabrication of electronic devices. The 2D perovskites/graphene photo detector inkjet printings use graphite films as a top contact. According to Tan, et al. [135] graphite has, in many cases, been found to be highly responsive (at about 2,100 A/W) with a very low dark current of about 1x 10$^{-8}$ Amperes which is achieved when an inkjet is designed with interdigital graphene electrodes.

According to Alamán [13], inkjet printing is conventionally used in graphics and has been investigated widely as a valuable tool for making practical devices and surfaces. In the past two decades, enormous effort has been made to develop materials that are solution-processable in the field of large-area devices for organic PV and display technology. [133] It has therefore been proved in the laboratory how efficiency, durability, as well as color gamut can be achieved to an excellent degree with fully
inkjet printing technology concerning devices incorporating QDs.\textsuperscript{[131]} The discovery of graphene triggered intensive research on two-dimensional materials which have been very transformational in the production of two-dimensional electronics. In their review \textsuperscript{[135]}, Xu et al. (2016) investigated the experimental effort involved in interfacing 2-D layers with 3-D materials to analyze the properties of the resultant heterojunctions. The combination of both the two-dimensional and three-dimensional semiconductors gave rise to a type of p-n junction that led to their debut. A review of the potential applications of each form of the heterojunction was also carried out. Focusing on the photoactive layer, bulk heterojunctions comprising a polymer conjugated with an electron donor as well as materials based on an electron acceptor fullerene, have attracted significant attention as the most promising approach to low-cost energy production. Research efforts done on inkjet printing consisting of different layered devices which focus on the photoactive materials have presented a powerful and fast experimental approach to improving the processing-structure properties relationship.

Besides its rapid fabrication process and low cost, inkjet printing exhibits an interesting advantage over traditional techniques, in that it has complex and high aspect-ratio geometries. It has been demonstrated that these printers have a feasible means to beam-shape the light from lasers of an edge emitting diode. On the other hand, micro lenses positioned precisely on top of a photo detector array can improve their light collecting efficiency.\textsuperscript{[131]} As a result, the inkjet printer has been very attractive for in situ micro lense preparation with optical input/output (I/O)
connections for robust high-speed switching or parallel information processing. Inkjet printing critically depends on the behavior of ejected printed drops occurring after an action of jetting. Past studies show that more viscous ink results in a higher onset bias. The fabrication of functional device structures through inkjet printing entails the use of pre-patterned substrates at some levels of processing and has the potential of involving multiple materials.

Direct printing on paper aims at cost-effectiveness as well as increased volume of applications. For instance, photovoltaics and electromagnetic shielding are biocompatible and recyclable. The inks that are composed of graphene/perovskite in a 2D inkjet printing photo detector use soluble graphite coupled with an active polymer (perovskite). Graphene is a carbon and the printing functionalization can be enhanced when its precursor has a high ratio of bulk carbon in order to achieve approximately 6% functional group weight. Graphene and perovskite inks are readily dispersed when they have a concentration of approximately 3 mg per liter in non-toxic solvents and are reported to be stable for months.

4.2 Results and Discussion

Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3-x\text{Cl}_x$ has an active layer which enables electrodes to produce maximum fabrication efficiency and synthesis for optimal optoelectrical performance. The process is sequential and systematic with four basic steps as illustrated in Figure 4-1.

The plain polycrystalline graphene first undergoes electrode cleaning to produce a high crystallinity size of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ (Figure 4-1(a)). The choice of the substrate is normally selected based on the ability of the printing technique particularly those which are
favorable for fabricating flexible devices. For maximum optoelectronic application and reduction of reflection of photons, glass was selected. The selected sample underwent surface treatment by use of an ultrasonic cleaning method utilizing ethanol and deionized water. This also served to ensure little corrosion and surface contamination of polycrystalline CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$.

The cleaned glass was then fixed on the printing platform, and CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ ink was injected into an ink-jet printer then annealed at 400°C (Figure 4-1(b)). This process was necessary to provide a straightforward means of improving the quality of sheets for optimal performance. Owing to the excellent dispersibility of CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$, the film was printed without difficulty.

Graphene electrodes were subsequently printed on the glass film. The print head was also heated at 60 °C. Moreover, the patterned graphene electrode was then subjected to sinter roasting by blowing for more than 10 minutes using a hairdryer to ensure further synthesis and the final product was annealed further at a curing temperature and produced the structure shown in Figure 4-1(d).

The product analysis of the electrical behavior portrays the characteristics shown in Figure 4-4. The photo detector current-voltage (I-V) characteristics were evaluated at 1000 mW/cm$^2$ under voltages from −3 to 3 V. This depicts ohmic contact formed between the perovskite and graphene electrodes which was the result of the energy adjustment after inkjet printing processed the graphene electrodes. In addition, there was an expectation that the current would increase gradually with increasing light intensity when
the same voltage is applied. At a bias of 3 V, the dark current was $1 \times 10^{-8}$ A at room temperature, and the photocurrent increased to 1 nA when the device was illuminated at a light power density of 1000 mW/cm$^2$ under vacuum. If the illumination intensity was increased further, we could expect a higher photocurrent to produce a large photocurrent on/off ratio. To the best of our knowledge, this is one of the best results among previous reports of perovskite-based lateral photo detectors. Optimizing experimental parameters, such as in Figure 4-2, demonstrates that stable single droplets can be obtained by controlling ink droplets while printing.

Glass substrates were cleaned by ultra-sonication in acetone, 2-propanol, and deionized (DI) water, successively. The substrates were dried with a nitrogen stream, followed by 30 seconds of oxygen plasma treatment. The active channels were 0.17922 cm in length and 0.95615 cm in width. The inkjet printing on substrates was accomplished to print interdigital electrodes using a DMP-2800 printer. First, the substrate was cut into required sizes and cleaned with acetone, isopropyl alcohol, and distilled water, and then dried with nitrogen. The contact electrodes were deposited on a square pad featuring different gaps (150 µm, 200 µm, 250 µm), and with interdigitated electrode design as demonstrated using Advanced Design System (ADS) Software (Figure 4-2). For the MSM photo detector, Au and Ag can be deposited by both thermal evaporation with a shadow mask or by inkjet printing, enabling us to compare the results. For the graphene-semiconductor-graphene (GSG) photo detector, the electrodes were deposited via the inkjet printer with the same geometrical characteristics. Finally, the photoactive layer was deposited by inkjet printing to completely cover the gap between the two electrodes to avoid short circuits. For
comparison, a control device was fabricated by inkjet printing with CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ precursor solution on the substrate.

Figure 4-1. The schematic illustration of the one-step printing process. A) Printing Graphene ink as interdigital electrodes. b) Graphene annealing at 400 °C as curing temperature in N2 environment. C) Printing perovskite ink as a photoactive layer on top of the interdigital electrodes and perovskite CH$_3$NH$_3$PbI$_3$-xCl$_x$ annealing at 90°C as curing temperature in air. D) The obtained films being annealed in an oven to form CH$_3$NH$_3$PbI$_3$-xCl$_x$ on graphene electrode.
Surface and morphological features of the MSM photo detector is characterized by scanning and transmission electron microscopy (SEM and TEM) to analyze the interface between the electrodes.

Figure 4-2. SEM (Scanning electron microscopy images) of perovskite and graphene synthesized with thin film perovskite and graphene.

The active area, CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$, morphology was characterized by scanning electronic microscopy (SEM, Nova Nano SEM 230). The photo luminescence spectra were recorded with a wavelength of 550 nm. X-ray diffraction spectra were collected with a Pert PRO diffractometer (PANalytical).
All the electrical parameters of the devices were measured with a semiconductor characterization system (Keithley, Model SCS-4200) assisted by a probe station. Monochromatic light was obtained with a xenon lamp at a wavelength of 630 nm, and a power meter was used to measure the light intensity. Electrical characterization of the photo detectors is described with and without light illumination using a semiconductor parameter analyzer. Wavelength-dependent electrical properties can also be determined using a broadband light emitting source, such as a Xe lamp.
Figure 4.4. Electrical characterization of the photo detector- Typical I-V characteristics of the perovskite/graphene printed photo detector device

4.3 Conclusion

The proposed concept is a promising technology for overcoming several significant challenges in inkjet printing of the emerging 2D layered materials. Combining the distillation assisted solvent exchange with polymer stabilization, we formulated stable, high concentration, environmentally friendly and printable inks for graphene, polycrystalline CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ and MoS$_2$. The inkjets produced excellent jetting performance and conformal and uniform printed patterns at a high resolution of tens of micrometers. They may also offer a general strategy to suppress the well-known and
often undesired coffee rings effects of inkjet printing. More importantly, this printing technology will allow for the fabrication of electronic devices in a simple method (typically several printing passes followed by simple annealing) but does not necessarily diminish the unique properties of 2D materials/perovskites using low-cost, scalable device fabrication techniques. This demonstrates that inkjet printer transparent conductors, supercapacitors, and photo detectors based on graphene have comparable or superior performance to those fabricated by other liquid phase techniques. In conclusion, our inkjet printing technology for 2D materials/perovskites using low-cost, scalable devices will substantially improve manufacturing efficiency and product quality. Our technology is therefore very promising for emerging organic and printed electronics.
Chapter 5

Conclusions and Future Research Work

5.1 Summary

In this work, we studied the mechanism of PHS heterojunction formation in single crystal stacking devices via ink jet printing using in situ fabrication techniques. We considered the roles of processing methods (FIB SEM for single crystal vs. ink jet printing for thin film) and conditions (thinning), type of semiconductor material, and ink formulation (choice of solvent additives) in the formation behavior of the PHS heterojunction used in photodetectors. Through the study of the mechanisms of PHS formation, we investigated the correlation between the process conditions of the PHS microstructure and photodetector performance. Moreover, our results demonstrated PHS compatible fabrication techniques while achieving high performance. In this chapter, we summarize the conclusions of this work and link our findings to the current and future challenges in the field of perovskite heterojunctions. Our research has resulted in the development of a general fabrication method for high-performance photo detectors. The motivation for this work was to gain a better understanding of a recently proposed technique using perovskite heterojunction for photo doctorates.

In this chapter, we summarize the primary contributions of this research and provide suggestions for future work in this area. The results obtained are summarized as follows:
In chapter 1, we demonstrated that PHSs uniquely combine the best optoelectronic properties that are required in heterostructure devices to obtain high efficiency performance compared to other thin-film heterostructures. This chapter provided a comprehensive overview of fabrication methods and explored recent advances in applications of PHSs. Moreover, the relationship between engineering PHSs, their performance in applications, and future challenges were discussed. The stability and surface interface architecture of the layer under the perovskite film in different materials were also considered. We also evaluated the steps required to optimize the interface parameters, including the interfacial work function alignment with perovskite, which can improve the transfer of charges and increase the open-circuit voltage of the device. However, high charge extraction and transport capacities that optimize perovskite film growth are necessary for effective interfacial properties. Furthermore, material properties such as ETL and HTL improve device stability. The many advantages of PHSs, namely simple solution processing and tunable optoelectronic properties, suggest these materials have a promising future.

In chapter 3, we demonstrated a new fabrication method for perovskite /MoS$_2$ single crystal as a novel approach using an FIB scanning electron microscope. Perovskite /MoS$_2$ single crystal is a promising research area for semiconductor optoelectronics. We conducted an investigation on perovskite and 2D MoS$_2$ single crystal as the n-type semiconducting materials, respectively. The current rectification behavior of the typical p-n junction can be clearly observed. We proceeded to summarize the optical and electronic mechanisms of the heterostructures. We can change the rectification ratio by tuning the gate voltage.
This device also shows photoresponse and fast response time. These results suggest a new direction in the design of optoelectronic devices based on layered inorganics and organics.

In chapter 4, we demonstrated the inkjet printing method to fabricate fully hybrid perovskite/graphene photo detectors, with balanced uniformity and low defect showing a clear photocurrent. The proposed concept is promising in the effort to overcome several significant challenges in inkjet printing of the emerging 2D layered materials. Combining the distillation assisted solvent exchange with polymer stabilization, we formulated stable, high concentration, environmentally-friendly and printable inks for graphene, polycrystalline CH$_3$NH$_3$PbI$_3$-$x$Cl$_x$ and MoS$_2$. The inkjets produce excellent jetting performance and conformal and uniform printed patterns at a high resolution of tens of micrometers. They may also offer a general strategy to suppress the undesired coffee rings effects in inkjet printing.

5.2 Future Research Work

Future work will focus on fabrication and characterization (CH$_3$NH$_3$PbBr$_3$ /MoS$_2$) of thin-film photo detectors using inkjet printing. We will also study the interface of CH$_3$NH$_3$PbBr$_3$/MoS$_2$ by simulation using QUATUMWISE ATK software via the fabrication process of the CH$_3$NH$_3$PbBr$_3$ perovskite /MoS$_2$ single crystal heterojunction.

Another future direction is partially printed CuO by inkjet printing as well as MoS$_2$ developed by CVD, and then the photo detection properties will be studied. Moreover,
in all of the systems studied herein, we investigated graphene ink properties to improve the conductivity for printed electrodes. There is a need for fabrication of all printed MoS$_2$ / graphene layers using MoS$_2$ and graphene ink prepared in the lab with complete ink and photodetector characterization. We expect to explore the mechanisms of printed film formation further and, to that end, interface simulation using QUATUMWISE ATK will be employed to study the fabrication process of the printed device (perovskite/graphene) thin-film photo detector. Furthermore, we will study time-dependent and wavelength-dependent photo detection measurements.

We anticipate that PHSs will be potential candidates for scalable manufacturing and the methods demonstrated in this work should continue to contribute to the understanding, controlling and scaling up of the processing of additional optoelectronic devices.
References


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