

Magneto-optical Effects in Multifunctional Materials

A Dissertation Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Hengxing Xu

May 2020

Copyright © 2020 by Hengxing Xu

All rights reserved.

Dedication

I dedicate this dissertation to my parents.

Acknowledgements

I would like to express my sincere gratitude to my Ph.D. dissertation advisor, Dr. Bin Hu, for the tremendous support and valuable advices in the past six years. I could not finish the dissertation without his dedication. I would also like to thank my graduate committee members, Dr. Tessa Calhoun, Dr. Zheng Gai, Dr. David Mandrus for their insightful and constructive comments on my dissertation.

I should devote my deep gratitude to my collaborators Dr. Ilia Ivanov, Dr. Valeria Lauter, Dr. Zheng Gai, Dr. Jong Keum, and Dr. Haile Ambaye at the Oak Ridge National Laboratory (ORNL) for their great help in providing facilities and discussions. I would also like to thank Dr. Kwang-Sup Lee, Dr. Prem Prabhakaran from Hannam University, and Dr. Tae-Woo Lee, Dr. Young-Hoon Kim from Seoul National University for providing samples and sharing me with their expertise in material engineering.

I owe my earnest thankfulness to my former lab's members, Dr. Mingxing Li, Dr. Yu-Che Hsiao, Dr. Qing Liu, Dr. Ting Wu, Dr. Lei He, Dr. Wei Qin, Dr. Mahshid Ahmadi, Dr. Shengbo Ma, and my current lab's members Miaosheng Wang, Jia Zhang, Yixuan Dou, Xixiang Zhu, Bogdan Dryzhakov. I would like to thank them for their numerous discussions and great support.

Finally, I particularly thank my parents and other family members in China for their unconditional support and encouragement.

Abstract

Multi-functional materials systems such as two-photon absorption based up-conversion crystals, magnetic/semiconducting hybrid 2D nanoparticles, and hybrid perovskites, have attracted significant research interest due to their exceptional magnetic-electronic-optical properties. However, the study of magneto-optical properties at room temperature with low field in these novel multi-functional materials is still lacking. The fundamental studies on the underlying mechanism of magneto-optical phenomenon based on excited states for these materials are still highly demanded. Magnetic field effects can be utilized as effective experimental tools to analyze spin-dependent processes of multi-functional materials in excited states. This thesis aims to experimentally explore the spin-dependent process in excited states for multi-functional materials toward improved performance, by using magnetic field effects and polarized photoexcitation. Chapter 1 presents a basic introduction to magnetic field effects and the development of metal-halide perovskites. Chapter 2 demonstrates magnetic field dependent photoluminescence based on multi-photon excitation in rare-earth nanocrystals by considering the spin-dependent electric dipoles. Chapter 3 illustrates photoexcitation-controllable magnetization based on a magnetic-semiconducting hybrid system by using steady-state pump-probe measurements in magnetic field. Chapter 4 studies the orbit-orbit interaction between polarized photoexcitation generated electron-hole pairs in metal halide perovskites and its influence on spin mixing process. In chapter 5, the dipole moment effect on light emission properties of metal halide perovskite nanoparticles by using cation doping will be demonstrated. Chapter 6 summarizes a conclusion for the entire studies in this dissertation.

Table of Contents

Chapter 1 Introduction	1
1.1 Introduction of Magnetic Field Effects	2
1.1.1 Formation of excited states.....	3
1.1.2 Spin mixing and spin conserving.....	4
1.1.3 Mechanism for magnetic field effects	5
1.2 Magneto-optical Effect in Excited States.....	9
1.2.1 Magneto-photoluminescence.....	9
1.2.2 Magneto-electroluminescence	10
1.2.3 Magneto-photocurrent	13
1.2.4 Magnetic field effect of light scattering	14
1.3 Metal Halide Perovskites	15
1.3.1 Recent progress in metal halide perovskites.....	15
1.3.2 Magnetic field effects in metal halide perovskites	17
1.3.3 Rashba effect in metal halide perovskite	18
1.4 Dissertation Outline.....	19
Chapter 2 Magneto-photoluminescence based on Two-photon Excitation in Lanthanide Doped Up-conversion Crystals.....	21
2.1 Abstract	22
2.2 Introduction	22
2.3 Materials and Methods	23
2.3.1 Sample preparation and characterization.....	23
2.3.2 Magneto-photoluminescence measurement	23
2.4 Results and Discussion.....	24

2.5 Summary	34
Chapter 3 Photoexcitation-controllable Magnetization in γ -Fe ₂ O ₃ -Graphene (0D-2D)	
Nanohybrids.....	35
3.1 Abstract	36
3.2 Introduction	36
3.3 Materials and Methods	37
3.3.1 Materials synthesis	37
3.3.2 Magnetic field effect of light scattering measurement	37
3.4 Results and Discussion.....	38
3.5 Summary	48
Chapter 4 Optically Tunable Spin-orbital Coupling Effects in Metal Halide Perovskites Solar Cell based on Polarized Photoexcitation.....	
4.1 Abstract	50
4.2 Introduction	50
4.3 Materials and Methods	51
4.3.1 Device fabrication.....	51
4.3.2 Characterization and magnetic field effect measurements	52
4.3.3 Polarization-dependent photocurrent and photoluminescence measurements	52
4.4 Results and Discussion.....	54
4.4 Summary	64
Chapter 5 Dipole Moment Effect on Light Emission Properties in Metal Halide Perovskite Nanoparticles	
5.1 Abstract	66
5.2 Introduction	66
5.3 Materials and Methods	67

5.3.1 Device fabrication.....	67
5.3.2 Measurement and characterization	69
5.4 Results and Discussion.....	70
5.5 Summary	79
Chapter 6 Conclusion.....	80
Reference	83
Vita.....	97

List of Figures

Figure 1- 1 Schematic of process and key parameters in magnetic field effect generation.....	6
Figure 1- 2 (a) (b) Effect of spin blocking during charge transport in bipolaron model.	8
Figure 1- 3 (a) Schematic of light emission process under photoexcitation. (b) Schematic of Δg mechanism for intersystem crossing, data adapted from ref 70.....	10
Figure 1- 4 (a) Schematic of electroluminescence process under electrical injection. (b) Schematic of recombination and intersystem crossing process in LEDs.	12
Figure 1- 5 (a) Schematic of the photocurrent generation in photovoltaic devices. (b) Magneto-photocurrent generated through field dependent intersystem crossing and triplet charge reaction channel.	13
Figure 1- 6 (a) Suspended nanoparticles with four dynamically balanced forces. (b) Randomly oriented nanoparticles are re-oriented according to the external magnetic field.	14
Figure 1- 7 Schematic diagram to show the structure of (a) 3D hybrid perovskite, (b) perovskite quantum dots, (c) layered quasi-2D perovskites.....	16
Figure 1- 8 (a) Magneto-photocurrent in the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ solar cell and (b) magneto-photoluminescence in $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ thin film. Data adapted from ref 76.	18
Figure 2- 1 Measurement setup for magneto-photoluminescence.	25
Figure 2- 2 (a) X-ray powder diffraction patterns of $\text{Y}_2\text{O}_2\text{S: Er, Yb}$. (b) SEM image of $\text{Y}_2\text{O}_2\text{S: Er, Yb}$ particles. (c) Up-conversion luminescence spectrum under different intensities 980nm IR laser excitation. (d) up-conversion emission intensity as a function of excitation intensity.	26
Figure 2- 3 (a) Magneto-photoluminescence of $\text{Y}_2\text{O}_2\text{S: Er, Yb}$ under high intensity 980nm IR laser excitation. (b) Magneto-photoluminescence of $\text{Y}_2\text{O}_2\text{S: Er, Yb}$ under high intensity 325nm laser excitation. (c) Down-conversion luminescence spectrum under different intensities 325nm laser excitation. (d) Down-conversion emission intensity as a function of excitation intensity...	29
Figure 2- 4 Magneto-photoluminescence generation in two photon up-conversion process by magnetically disturbing the balance of population of transition dipoles with different spin states.	30

Figure 2- 5 (a) Magneto-photoluminescence of Y_2O_2S : Er, Yb and $NaYF_4$: Er, Yb under high intensity 980nm IR laser excitation. (b) Normalized magneto-photoluminescence characteristics under 325nm and 980nm photoexcitation.....	32
Figure 2- 6 (a) Up-conversion luminescence spectrum of $NaYF_4$: Tm, Yb under different intensities 980nm IR laser excitation. (b) Magneto-photoluminescence of $NaYF_4$: Tm, Yb under high intensity excitation. (c) Normalized magneto-photoluminescence of different up-converting materials under $3640mW/cm^2$ 980nm photoexcitation.....	33
Figure 3- 1 (a) Schematic of self-assembled MYG nanohybrid. (b) Measurement setup of magnetic field effect of light scattering.	38
Figure 3- 2 (a) TEM image to show the morphology of magnetic nanoparticle functionalized graphene (MYG). The inset shows the chemical structure of ligand Y. (b) Schematic setup for measuring magnetic field effect of light scattering (MFE _{LS}) in excited state. (c) UV-vis absorption spectrum of MYG, ligand (Y), as synthesized magnetic nanoparticles (MNP) and electrolytically exfoliated graphene.	40
Figure 3- 3 (a) MFE _{LS} signals from magnetic nanoparticle functionalized graphene suspended in NMP with a concentration of 1mg/ml. (b) Time-dependent MFE _{LS} profile under different magnetic field (c) MFE _{LS} signals from the coupled sample (MFG) and separated components (MNP, graphene, organic molecules). (d) MFE _{LS} signals from MNP functionalized graphene in ground state and excited state. MFE _{LS} signals from (e) magnetic nanoparticles and (f) graphene.	43
Figure 3- 4 (a) MFE _{LS} signals from MYG in ground and excited states, (b) normalized MFE _{LS} curve of MYG in ground state and excited state. Time-dependent profile of MFE _{LS} signals from MYG under (c) ground state and (d) excited state.....	46
Figure 3- 5 (a) MFE _{LS} signals from MFG with MNP added. (b) normalized MFE _{LS} curves of MFG with MNP added. (c) MFE _{LS} signals from graphene with MNP added. (d) normalized MFE _{LS} curves of graphene with MNP added.	47
Figure 4- 1 (a) schematic diagram of perovskite solar cell. (b) Energy level diagram of perovskite solar cell. (c) Schematic of magnetic field effect measurements.	53

Figure 4- 2 Measurement setup for polarization-dependent Jsc and PL in metal halide perovskites by switching photoexcitation polarization.....	54
Figure 4- 3 (a) Device structure of MAPbI ₃ based solar cell. (b) Current-voltage characteristics of MAPbI ₃ based solar cell. (c) Absorption and photoluminescence spectrum of MAPbI ₃ thin film.....	55
Figure 4- 4 Normalized MFE _{PC} curves of MAPbI ₃ based solar cells under linear and circular excitation (a) 48mW/cm ² , (b) 120mW/cm ² , (c) 240mW/cm ² , (d) Normalized MFE _{PC} curves of MAPbI ₃ and MAPb _{0.5} Sn _{0.5} I ₃ based solar cells under 48mW/cm ² photoexcitation.....	58
Figure 4- 5 (a) Short-circuit current density of MAPbI ₃ solar cells recorded by switching photoexcitation polarization at 48mW/cm ² . (b) Schematic diagram of polarization dependent photocurrent. (c) Short-circuit current density of MAPbI ₃ solar cells recorded by switching photoexcitation polarization at 120mW/cm ² (d) Excitation intensity dependence of ΔJsc between linearly polarized excitation and circularly polarized excitation in MAPbI ₃ solar cells.	60
Figure 4- 6 (a) MFE _{PC} curves of organic solar cells with device structure of ITO/PFN/PCBM: PTB7/MoO ₃ /Ag under different polarized photoexcitations. (b) Short-circuit current density of organic solar cells recorded by switching photoexcitation between linearly polarized light and circularly polarized light excitation at 120mW/cm ² . (c) Short-circuit current density change of organic solar cells by switching light polarization as a function of photoexcitation intensity.	62
Figure 4- 7 (a) Photoluminescence intensity of MAPbI ₃ thin film on a quartz substrate recorded by switching photoexcitation between linearly polarized excitation and circularly polarized excitation at 120mW/cm ² . (b) Transient absorption spectra of MAPbI ₃ thin film on a quartz substrate at different delay times up to 1 ps. (c) PL lifetime of MAPbI ₃ thin film on a quartz substrate.	63
Figure 5- 1 (a) schematic diagram of perovskite light emitting diode. (b) Energy level diagram of perovskite light emitting diode.	68
Figure 5- 2 Time-resolved photoluminescence anisotropy measurement setup.	69
Figure 5- 3 (a) Photoluminescence spectrum of undoped and GUA doped FAPbBr ₃ nanoparticle thin films. (b) FAPbBr ₃ nanoparticle size with different GUA doping concentration.	71

Figure 5- 4 (a) Polarization dependent photoluminescence of FAPbBr ₃ nanoparticle thin film with 100mW/cm ² photoexcitation. (b) Polarization dependent photoluminescence of GUA doped FAPbBr ₃ nanoparticle thin film with 100mW/cm ² photoexcitation. (c) Schematic diagram of linear/circular photoexcitation modulated photoluminescence in perovskites.	73
Figure 5- 5 (a) PL intensity change by switching photoexcitation polarization as a function of excitation intensity for GUA doped FAPbBr ₃ nanoparticle thin films. (b) PLQE of undoped and 10% GUA doped FAPbBr ₃ nanoparticle thin films.	75
Figure 5- 6 (a) PL lifetime of undoped and GUA doped FAPbBr ₃ nanoparticles. (b) PL anisotropy decay of FAPbBr ₃ nanoparticles, (c) PL anisotropy decay of GUA doped FAPbBr ₃ nanoparticles.	77
Figure 5- 7 (a) Electroluminescence spectrum of FAPbBr ₃ nanoparticle LEDs with different GUA dopant concentration. (b) Luminance characteristics of FAPbBr ₃ nanoparticle LEDs.....	78

Chapter 1 Introduction

1.1 Introduction of Magnetic Field Effects

Magnetic field effects (MFEs) refer to the phenomena where magnetic field can change the properties of excited states in photoluminescence, electroluminescence, charge transport, photocurrent, etc. and have been intensively studied during the recent years. The magnetic field effects are defined as:

$$MFE = \frac{S_B - S_0}{S_0} \quad (1-1)$$

where S_0 and S_B are signals without and with external magnetic field. In the 1960s and 1970s, early study on MFEs showed that the interaction between spin dependent excitons can be influenced by low magnetic field (~ 500 mT) in organic materials¹⁻³. Due to the development of organic electronics, MFEs have attracted extensive research effort, since the first demonstration of magneto-resistance in organic spin valve in early 2000s⁴. During that time, MFEs were demonstrated based on spin-dependent charge recombination, dissociation and charge transport in organic semiconductors and organic electronic devices⁵⁻²¹. In 2003, Kalinowski et al. found that the electroluminescence intensity and current of Alq_3 based light emitting diode (LED) can be increased by 5% and 3% under applied magnetic field up to 300 mT, respectively²². In 2005, Mermer et al. reported large magneto-resistance observed in both small molecule and π -conjugated polymers without ferromagnetic electrode at room temperature²³. Photocurrent change in PPV (*p*-phenylene vinylene) thin film under low magnetic field was reported by Frankevich²⁴. In 2013, Zang et al. have reported that electric polarization at donor: acceptor interface can be changed by external magnetic field based on photoexcitation generated charge transfer states²⁵. Recently, He et al. reported scattered light intensity from two-dimensional nanoparticle suspension can be changed by external magnetic field²⁶.

Based on both theoretical and experimental studies, the understanding of key processes and parameters in determining MFEs has been improved. Specifically, the external magnetic field can influence the spin mixing induced by spin orbital coupling (SOC) and hyperfine interaction (HFI), and spin conserving due to exchange interaction, leading to redistribution of population of spin dependent excited states, leading to magnetic field dependent properties. Different from the MFEs in spin valves, the MFEs based on excited states can be realized without incorporation of magnetic structures under low magnetic field at room temperature, which makes MFEs a practical method

to analyze the spin dependent charge behaviors in organic semiconductors and devices. Nevertheless, since MFEs can reveal the spin and energy parameters in excited states, they can provide insight for materials synthesis and device structure design to achieve improved performance.

To get insightful understanding on spin-dependent process in newly emerging materials systems, such as metal halide perovskites, 2D materials, and develop new mechanisms to control their magnetic, electronic and optical properties, research effort is highly demanded in the fundamental understanding of MFEs. The following review section will mainly focus on the key process in generation of MFEs, the development of magneto-optical phenomena, and magneto-optical properties of new materials system.

1.1.1 Formation of excited states

Upon photoexcitation and electrical injection, excited states can be formed in semiconductors in different forms including exciton, charge transfer state, polaron pair, exciplex. Excitons can be classified as Wannier type and Frenkel type according to their electron-hole binding energy and separation distance. Wannier exciton forms in semiconductors with large dielectric constant, leading to loosely bounded electron hole with typical binding energy around 0.01eV and large Bohr radius. Whereas, Frenkel exciton can be formed in organic semiconductors with small dielectric constant, with typical binding energy on the order of 0.1 to 1 eV and small Bohr radius. Excitonic states can dissociate into spatially separated charges at donor-acceptor interface to form charge-transfer states. Generally, Organic materials are less rigid than inorganic materials. Thus, the charge carrier propagation in organic materials can lead to distortion of host materials and consequently form a quasi-particle called a polaron. A polaron pair is a coulombic bounded pair of two oppositely charged polarons formed on two adjacent chains. Polaron pair can relax to form a tightly bonded state with lower energy called an exciplex.

Excited states can also be classified by their spin configuration. When electron and hole with randomly oriented spin come into contact, they can either form a singlet or a triplet state. In optical excitation, singlet excited states are formed due to the spin selection rule. In electrical excitation, the electrically injected electrons and holes can form singlet exciton and triplet exciton

with the ratio of 1:3 through random capture process based on the spin statistics^{27, 28}, as shown in equation 2.

$$\begin{aligned}
e \uparrow e \downarrow + h \uparrow h \downarrow &\rightarrow \frac{1}{4} e \uparrow h \downarrow + \frac{1}{4} e \downarrow h \uparrow + \frac{1}{4} e \uparrow h \uparrow + \frac{1}{4} e \downarrow h \downarrow \\
&\rightarrow \frac{1}{4} (|e \downarrow h \uparrow\rangle - |e \uparrow h \downarrow\rangle) + \frac{1}{4} (|e \downarrow h \uparrow\rangle + |e \uparrow h \downarrow\rangle) + \frac{1}{4} |e \uparrow h \uparrow\rangle + \frac{1}{4} |e \downarrow h \downarrow\rangle \\
&\rightarrow \frac{1}{4} S_{m=0} + \frac{1}{4} T_{m=0} + \frac{1}{4} T_{m=1} + \frac{1}{4} T_{m=-1}
\end{aligned} \tag{1-2}$$

1.1.2 Spin mixing and spin conserving

Spin mixing refers to the conversion between different spin states, which requires spin flipping to occur. Spin flipping in most solids is mainly caused by internal magnetic interaction such as spin-orbital coupling (SOC) and hyperfine interaction (HFI). In this process, the initial spin polarization gradually decays to random, leading to spin relaxation. Spin conserving refers to the process where the spin states intend to keep their original spin configurations. In any spin dynamic process, the energy and spin momentum should be conserved simultaneously. Due to the difference in energy and spin momentum between singlet and triplet states, the conversion of different spin states needs to satisfy both energy and spin momentum conservation. The energy difference between singlets and triplets (ΔE_{ST}) is decided by the exchange interaction within the excited states. Generally, exchange interaction is mainly responsible for the spin conserving process. Here, the spin mixing and spin conserving processes will be briefly introduced.

SOC originates from the interaction between the electron's spin and its orbital motion around an atomic nucleus. In atomic physics, the relativistic Hamiltonian of electron motion can have a term H_{SO} that couples electron's spin s with orbital l in atom i :

$$H_{SO} = \sum \lambda_i \mathbf{l}_i \cdot \mathbf{s}_i \tag{1-3}$$

where λ_i is the atomic SOC strength. For a nucleus with charge Ze , $\lambda \propto Z^4$, where Z is the atomic number. Thus, the SOC strength becomes stronger in systems with heavier atoms. Organic materials composed of light elements with small atomic SOC, such as C, H, O, and N, have very

weak SOC. Many organic materials studied for spintronic applications also contain heavier elements, Al in tris-(8-hydroxyquinoline) aluminum (Alq3), Cu in copper phthalocyanine (CuPc), which have stronger atomic SOC.

HFI describes the magnetic interaction between the electron spin and the spin of proton nucleus. HFI widely exists in organic materials. Comparing with SOC, HFI is relatively weak, that can be overcome by external magnetic field up to 10mT. Early research studied the isotope effects on spin dynamics in π -conjugated polymer by replacing H with D. The polymer with deuteration shows a narrower curve-shape in magnetic field effect, indicating a weaker HFI strength⁶. This observation confirms that the HFI is generated via interaction between electron spin and nucleus spin. The HFI dependent spin dynamics in organic semiconductors, suggests the important role of HFI in the generation of magnetic field effects and spin transport.

Exchange interaction is responsible for spin conserving that prevent spin flipping process in polaron pairs and excitons. It is generated from electrostatic Coulomb interaction between electron and hole with wavefunction overlap. The exchange interaction can be described as:

$$J(r_e, r_h) = J_0 \exp[-\alpha(r_e - r_h)] \quad (1-4)$$

where J_0 is a radius constant, α is the exchange interaction strength, r_e and r_h are the spatial position of electron and hole, respectively. Exchange interaction is highly dependent on the separation distance between electron and hole. In Frenkel excitons with short electron hole separation distance, the exchange interaction is relatively strong. Spin mixing is disallowed by the strong exchange interaction. Wannier type excitons are spatially extended with large Bohr radius, leading to relatively small exchange interaction. Internal magnetic interaction, such as HFI and SOC, can compete with exchange interaction, generating spin mixing between singlet and triplet states. The exchange interaction can also be modified by the density of excited states via Coulomb screening effect.

1.1.3 Mechanism for magnetic field effects

1.1.3.1 Polaron pair model (electron-hole pair model)

In polaron pair state (electron-hole pair), the exchange interaction is relatively small. The spins of electron and hole in excited states can flip under the influence of internal magnetic field

induced by SOC and HFI, leading to intersystem crossing (ISC) through spin mixing between singlet states and triplet states. Meanwhile, the exchange interaction can serve as spin conserving process that competes with spin mixing. The competition between exchange interaction and internal magnetic interactions leads to equilibrium on the populations of singlet and triplet states. When an applied magnetic field can be comparable to the internal magnetic field or exchange interaction, equilibrium in singlet/triplet ratio can be disturbed leading to a change in the population of singlet and triplet states. Since singlet and triplet excited states have different recombination rates, dissociation rates and wavefunctions (**Figure 1-1**). When the singlet/triplet ratio is modified by an external magnetic field, the magnetic field dependent photoluminescence, electroluminescence, photocurrent, and dielectric phenomena can be generated consequently. Here, the magnetic field effects discussed in this thesis are mainly based on polaron pair model.

1.1.3.2 Exciton model

Excitons exhibit strong exchange interaction, which disallowing spin mixing between singlet and triplet states. During exciton diffusion in organic semiconductors, exciton inevitably collide with each other, or with free carriers and trapped charges, leading to exciton-exciton

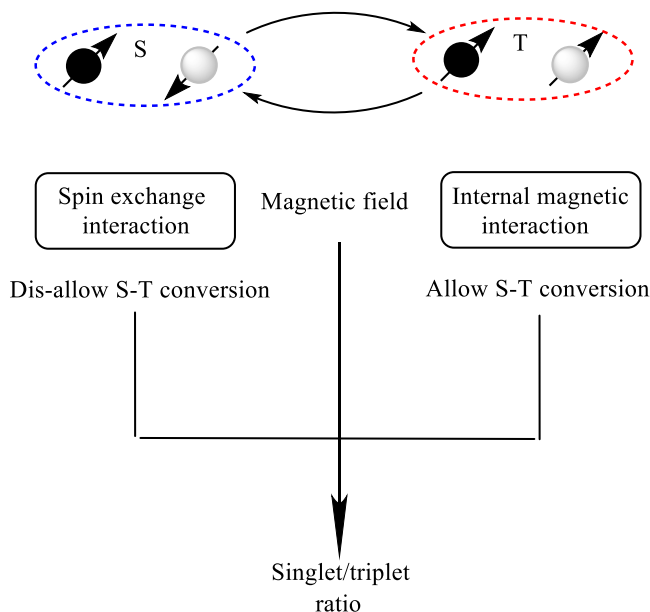


Figure 1- 1 Schematic of process and key parameters in magnetic field effect generation.

interaction and exciton-charge interaction. Theoretically, both singlet exciton and triplet exciton can contribute to the reactions. Nonetheless, due to the longer lifetime of triplet exciton, exciton-exciton interaction and exciton-charge interaction are dominated by triplet excitons, namely triplet-triplet annihilation (TTA) and triplet-charge annihilation (TCA).

In the TTA process, two triplet excitons can interact with each other to form an excited singlet and a ground singlet. The process can be expressed as:



where ${}^1T_{\uparrow\uparrow}$ and ${}^1T_{\downarrow\downarrow}$ are the triplet excited states, ${}^1S_{\uparrow\downarrow}$ is the singlet excited state, and ${}^0S_{\uparrow\downarrow}$ is the ground state²⁹. Delayed fluorescence can be generated by the excited singlet through TTA. An external magnetic field may perturb the triplet-triplet annihilation rate, leading to a magnetic field dependent light emission³⁰.

In the TCA process, free charge carrier or trapped charge carrier interacts with triplet exciton and breaks triplet exciton into free charge carriers. The free charge carrier generated from TCA can undergo dissociation that contributes to electric current, or recapture to form light-emitting singlet state. An external magnetic field can disturb the spin interaction between a triplet exciton and a charge in triplet-charge reaction leading to a change in triplet-charge reaction rate constant^{31, 32}. Therefore, magnetic field dependent electric current or magnetic field dependent electroluminescence can be realized based on the TCA process.

1.1.3.3 Bipolaron model

Early studies have shown that organic magneto-resistance (OMAR) can be observed in unipolar injection organic light emitting diode with nonmagnetic electrode. Since excited states cannot be formed with single carrier charge injection, the observed OMAR can be attributed to magnetic field dependent charge mobility phenomenon. The OMAR can be generated at low magnetic field (10mT) at room temperature with large amplitude (more than 10%). Furthermore, the sign of OMAR can be switched between positive and negative dependent on materials and working conditions. The OMAR can be generated through: i) different types of charged particles (polaron and bipolaron) formation with magnetic field dependent interconversion, ii) difference in mobility of different charged particles. Based on bipolaron mechanism, considering a charge

carrier (polaron) hops to a site filled with a trapped polaron, singlet bipolaron can be formed when they have opposite spins leading to no blockage for charge transport. Otherwise, the polaron will be blocked since it's much higher in energy to form bipolaron with triplet spin configuration, as shown in **Figure 1-2**. The spins of the polarons precess about their random hyperfine field can cause spin mixing leading to the formation of singlet bipolaron. An external magnetic field with strength stronger than the hyperfine field, can introduce coherent precession along the applied field leading to reduced spin mixing, and consequently, reduce the bipolaron formation probability¹¹. Thus, positive magneto-resistance can be observed due to the enhanced spin blocking. On the other hand, the density of polaron can be increased when the formation of bipolaron is reduced under magnetic field. It is known that polaron and bipolaron high and low mobility due to their different lattice distortion. Therefore, the reduction of bipolaron formation can increase the number of polarons leading to an increase in current, and consequently producing a negative magnetoresistance.

1.1.3.4 Δg model

Δg model is based on that positive and negative polarons have different g -factors. In singlet and triplet states, positive and negative polarons precess differently around the applied magnetic field, with Larmor frequencies. The difference in frequency can be described as:

$$\Delta\omega_p = \mu_B \Delta g B / \hbar \quad (1-6)$$

where μ_B is the Bohr magneton, B is the applied magnetic field strength, $\hbar$ is the Planck's constant

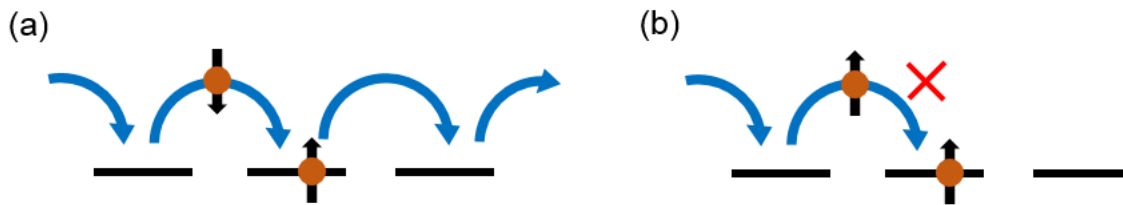


Figure 1- 2 (a) (b) Effect of spin blocking during charge transport in bipolaron model.

where μ_B is the Bohr magneton, B is the applied magnetic field strength, $\hbar$ is the Planck's constant, $\Delta g = g_e - g_h$ is the difference in g-factor of positive and negative polarons^{33, 34}. When the external magnetic field is strong enough, the large spin precession frequency difference between positive and negative polarons may lead to intersystem crossing between singlet and triplet states, and consequently change the singlet/triplet ratio. In a material system that singlet and triplet contribute differently to the light emission or charge dissociation, magnetic field dependent luminescence or current can be observed.

1.2 Magneto-optical Effect in Excited States

1.2.1 Magneto-photoluminescence

Magneto-photoluminescence refers to the phenomenon that photoluminescence intensity is changed by an applied magnetic field. In semiconductor, electron can be excited into a higher excitonic state when a photon with energy higher than the bandgap is absorbed. After rapid thermalization, a photon can be re-emitted as the electron returns to the lower energy state (**Figure 1-3a**). Basically, singlet excited states can be generated under photoexcitation due to spin selection rule, then the singlet excited states can convert to triplet excited states through spin-flipping mechanism, leading to a dynamic equilibrium in singlet-triplet population ratio. When a magnetic field changes the singlet and triplet population ratio, magneto-photoluminescence can be observed due to the different recombination rates of singlet and triplet excited states.

In general, magneto-photoluminescence can be realized in two different mechanisms: (i) manipulating electron spins towards the formation of spin-dependent excited states and (ii) redistributing the populations between different spin-dependent excited states. Experimental studies have shown that the manipulating electron spins towards the formation of spin-dependent excited states requires large magnetic field at low temperature or incorporation of magnetic structures, in order to overcome the thermal energy. On contrast, re-distributing the populations between different spin-dependent excited states can be realized without magnetic structures at low field and room temperature. Generally, when excited states are formed with long electron hole separation distance resulting in weak exchange interaction, intersystem crossing due to HFI or SOC can occur and compete with exchange interaction leading an equilibrium in singlet-triplet population ratio. When an applied magnetic field can disturb the equilibrium, magneto-

photoluminescence can be observed through field dependent intersystem crossing. Besides, the deviation of Lande's g factor was considered a feasible mechanism to generate magneto-photoluminescence in excited states. The g factors of positive and negative polarons can be differently deviated as compared to free electrons leading to different Larmor frequencies towards field-dependent spin mixing, namely Δg mechanism generating intersystem crossing³⁵ (**Figure 1-3b**). However, the Δg for organic semiconductors are in the range of 10^{-2} - 10^{-3} , thus the Δg mechanism can be only available under larger magnetic field ^{36, 37}($>1\text{T}$).

Magneto-photoluminescence can be used as an effective experimental tool to investigate the spin dependent excited states formation, charge dissociation and recombination process of semiconductors. Furthermore, exploring the fundamental mechanism of the magneto-photoluminescence in various light emitting materials can lead to the development potential application of light and magnetic field sensing and field controllable displays.

1.2.2 Magneto-electroluminescence

Magneto-electroluminescence refers to the magnetic field induced change on the electroluminescence in light-emitting devices through electrically formed excited states. It has

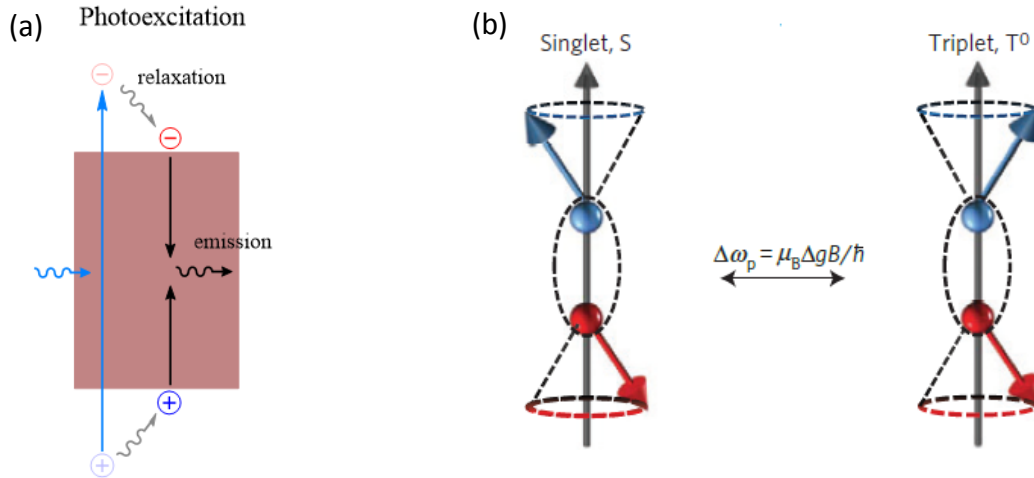


Figure 1- 3 (a) Schematic of light emission process under photoexcitation. (b) Schematic of Δg mechanism for intersystem crossing, data adapted from ref 70.

been extensively demonstrated in organic light emitting diodes, and still attract much attention due to its importance in analyzing spin dependent light emission process in newly emerging light emitting materials such as TADF molecules. In general, the working principle of OLEDs includes four essential processes: (1) injection of charge carriers from electrodes; (2) transport of charge carriers under electric field; (3) formation of bound electron-hole pairs as excited states; (4) radiative recombination of excitons as shown in **Figure 1-4a**.

During the operation, the electrons and holes are injected into the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of organic light emitter, respectively. When the distance of oppositely charged carriers is within the Coulomb capture radius they can form loosely bound electron-hole pairs such as polaron pairs, CT states, and exciplex states. Consequently, the electron-hole pairs can evolve into closely bound excited states due to the Coulombic attraction leading to light emitting excitons. The radiative recombination of these excitons generates the electroluminescence. Generally, the external magnetic field can influence the population ratio of spin dependent excited states in their loosely bound electron-hole pair form. It is known that random capture of electrically injected electrons and holes generates 25% spin antiparallel states and 75% spin parallel states based on spin statistics. The intersystem crossing between singlet states and triplet states can happen within the electron-hole pairs due to the relatively small exchange interaction^{38, 39}. An external magnetic field can change the intersystem crossing in electron-hole pairs, leading to the change in singlet/triplet ratio (**Figure 1-4b**). As a consequence, magneto-electroluminescence is generated due to the different recombination rates of singlet and triplet states.

Magneto-electroluminescence has been proven as a practical tool in analyzing spin dependent process including charge transport and recombination in organic light emitting materials. The development of magneto-electroluminescence can facilitate the studies on improving light emission efficiency and avoiding non-radiative recombination loss, thus offers a new guideline for light emitting device design.

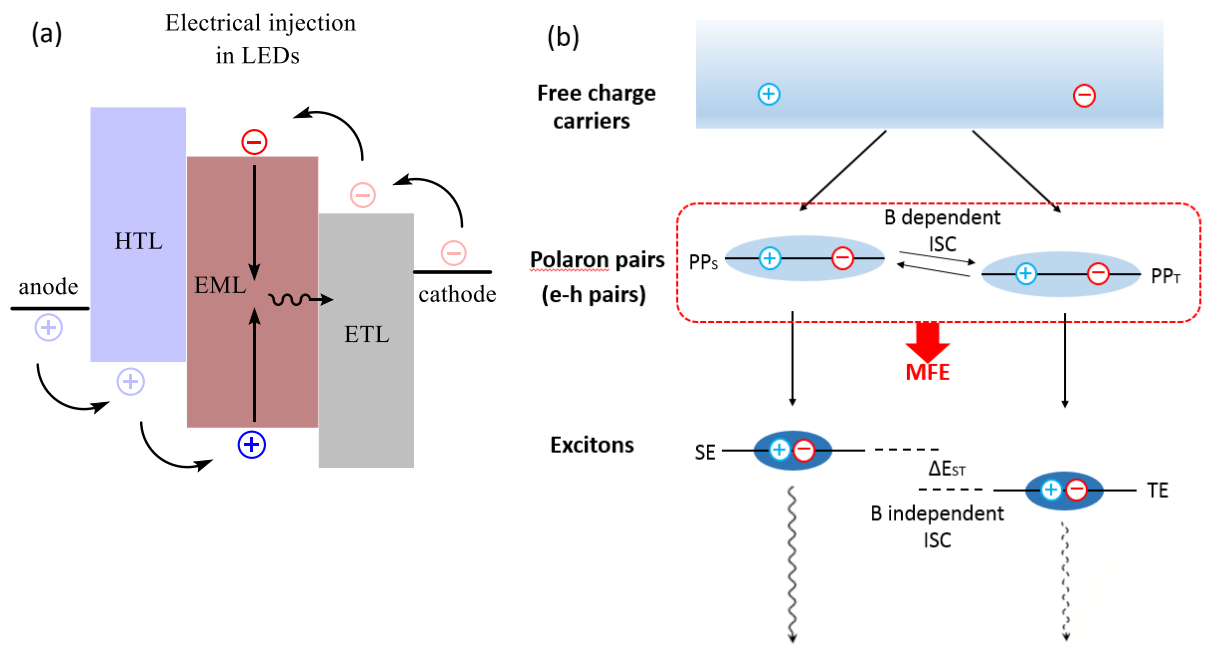


Figure 1- 4 (a) Schematic of electroluminescence process under electrical injection. (b) Schematic of recombination and intersystem crossing process in LEDs.

1.2.3 Magneto-photocurrent

In organic semiconductors, an external magnetic field can change electric current generated by the photoexcited states leading to magneto-photocurrent. Basically, photocurrent generation is composed of four processes: light absorption, formation of excited states, charge carrier generation from excited states, charge carriers transport in semiconductors (**Figure 1-5a**). Among these processes, an applied magnetic field can influence charge carriers generation from excited states, leading to a magnetic field dependent photocurrent⁴⁰. Therefore, magneto-photocurrent can be used as a useful experimental approach to explore the dissociation, interaction and recombination process of excited states in solar cells under working condition^{15, 41, 42}.

There are two main channels, namely exciton dissociation, and exciton charge reaction, to convert photoexcited states into photocurrent in solar cells. Basically, singlet excitons are first generated due to the spin selection rule under photoexcitation. Singlet excitons can also dissociate into weakly Coulombic bounded singlet electron-hole pairs. Meanwhile, singlet electron-hole pairs can be partially converted into triplet electron-hole pairs through ISC caused by internal magnetic interaction such as hyperfine interaction (HFI) and spin-orbital coupling (SOC), leading to

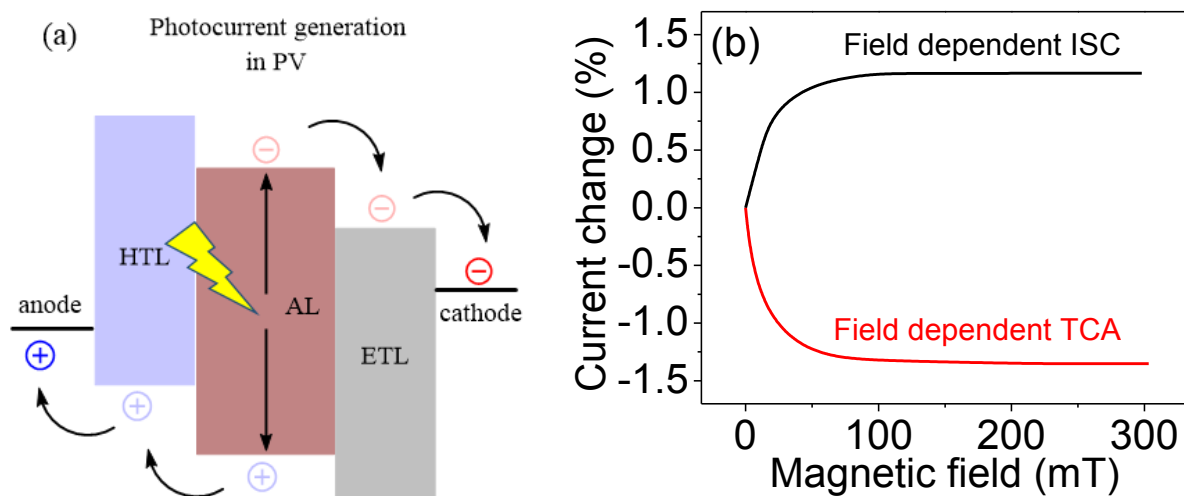


Figure 1- 5 (a) Schematic of the photocurrent generation in photovoltaic devices. (b) Magneto-photocurrent generated through field dependent intersystem crossing and triplet charge reaction channel.

coexistence of singlet and triplet electron-hole pairs. For the dissociation channel, magnetic field can shift the singlet-triplet electron-hole pairs population ratio by introducing spin precession, consequently change the photocurrent due to different dissociation rates. For the exciton-charge reaction channel, the exciton-charge reaction occurs mainly through Coulombic scattering between an excited state and a charge carrier resulting in excited states breaking into charge carriers^{43, 44} or releasing the trapped charge carriers⁴⁵⁻⁴⁷. Triplets can dominate the exciton charge reaction process when experiencing sufficient physical contact with charge carriers due to their relatively long lifetime (**Figure 1-5b**).

1.2.4 Magnetic field effect of light scattering

Magnetic field effect of light scattering (MFE_{LS}) refers to the phenomenon that the scattered light intensity from certain mediums such as nanoparticle suspension can be changed by an external magnetic field. Magnetic field effect of light scattering is a new member of the magnetic field effect family, which has been observed from diamagnetic and ferromagnetic nanoparticles suspended in solvents⁴⁸. And it has been proved to be an effective experimental method to study the dynamic magnetization and field-induced structure change in nanoparticle suspension⁴⁹⁻⁵¹.

Basically, in suspensions, the suspended particles experience four dynamically balanced forces: gravitation, floatation, molecular collision, and solvent dielectric interaction, which can lead to even distribution of suspending particles in a solvent with random orientation (**Figure 1-6a**).

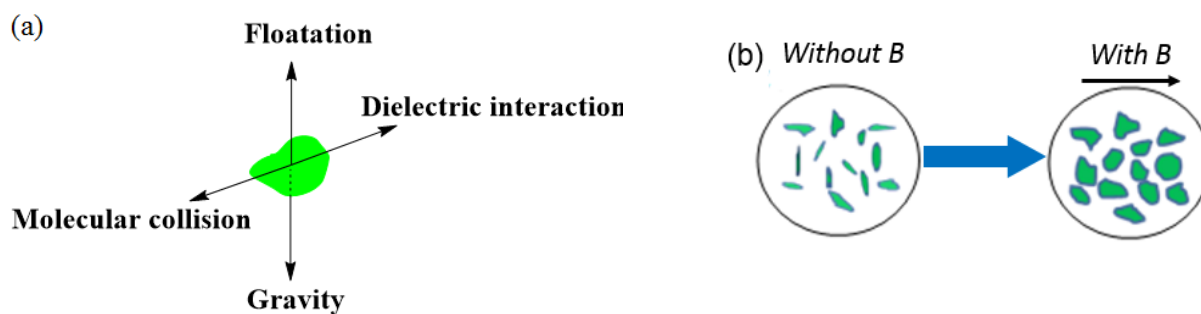


Figure 1- 6 (a) Suspended nanoparticles with four dynamically balanced forces. (b) Randomly oriented nanoparticles are re-oriented according to the external magnetic field.

An applied magnetic field can induce anisotropic magnetization in the suspended particles, and cause re-orientation for suspended particles by breaking the dynamic equilibrium of suspension (shown in **Figure 1-6b**). As a consequence, the light scattering cross-section from the suspended particles is significantly changed generating a magnetic field dependent scattered light intensity²⁶.

1.3 Metal Halide Perovskites

1.3.1 Recent progress in metal halide perovskites

Metal halide perovskites (MHPs) (with structure ABX_3 , where $A=Cs^+$, $CH_3NH_3^+$, $HC(NH_2)_2^+$; $B=Pb^{2+}$, Sn^{2+} ; $X=Br^-$, I^- , Cl^-) have recently emerged as promising materials for solution-processed optoelectronic applications such as photovoltaics⁵²⁻⁵⁴, light-emitting diodes⁵⁵⁻⁵⁷, photodetectors⁵⁸⁻⁶⁰ and lasers⁶¹⁻⁶³ (**Figure 1-7a**).

The metal halide perovskite-based photovoltaics have made impressive progress in the past few years with maximum power conversion efficiency jumping from 3.8% in 2009⁶⁴ to over 23% in 2019⁶⁵. The superior performances of perovskite photovoltaics have been attributed to their high carrier mobility, large light absorption coefficient in the visible range, and long charge carrier diffusion length in the micrometer range. MHPs have also been proven to be good light emitters, with tunable emission color, narrow spectral width. The external quantum efficiency (EQE) of MHPs LEDs has increased from 0.1% to 11.7% in three years^{66, 67}. Besides, optical pumped lasing has been achieved in MHPs polycrystalline films, and single crystals, with low lasing threshold, and high optical gain⁶⁸.

However, 3D MHPs suffer from thermo/moisture instability, low recombination rate, and low exciton binding energy which are unfavorable for optoelectronic applications, especially for the light emitting purpose. By substituting methylammonium (MA) cations with long organic cations such as octylamine (OA), phenylethylammonium (PEA), the crystal structures of perovskites change to quasi-2D layered structures. The quasi-2D perovskites are composed of different numbers of PbX_6 ($X=Br^-$, I^- , Cl^-) monolayer, sandwiched between long organic cations as spacer (**Figure 1-7c**). Quasi-2D perovskites can exhibit large exciton binding energy due to strong quantum confinement, much better stability compared to their 3D counterpart with the

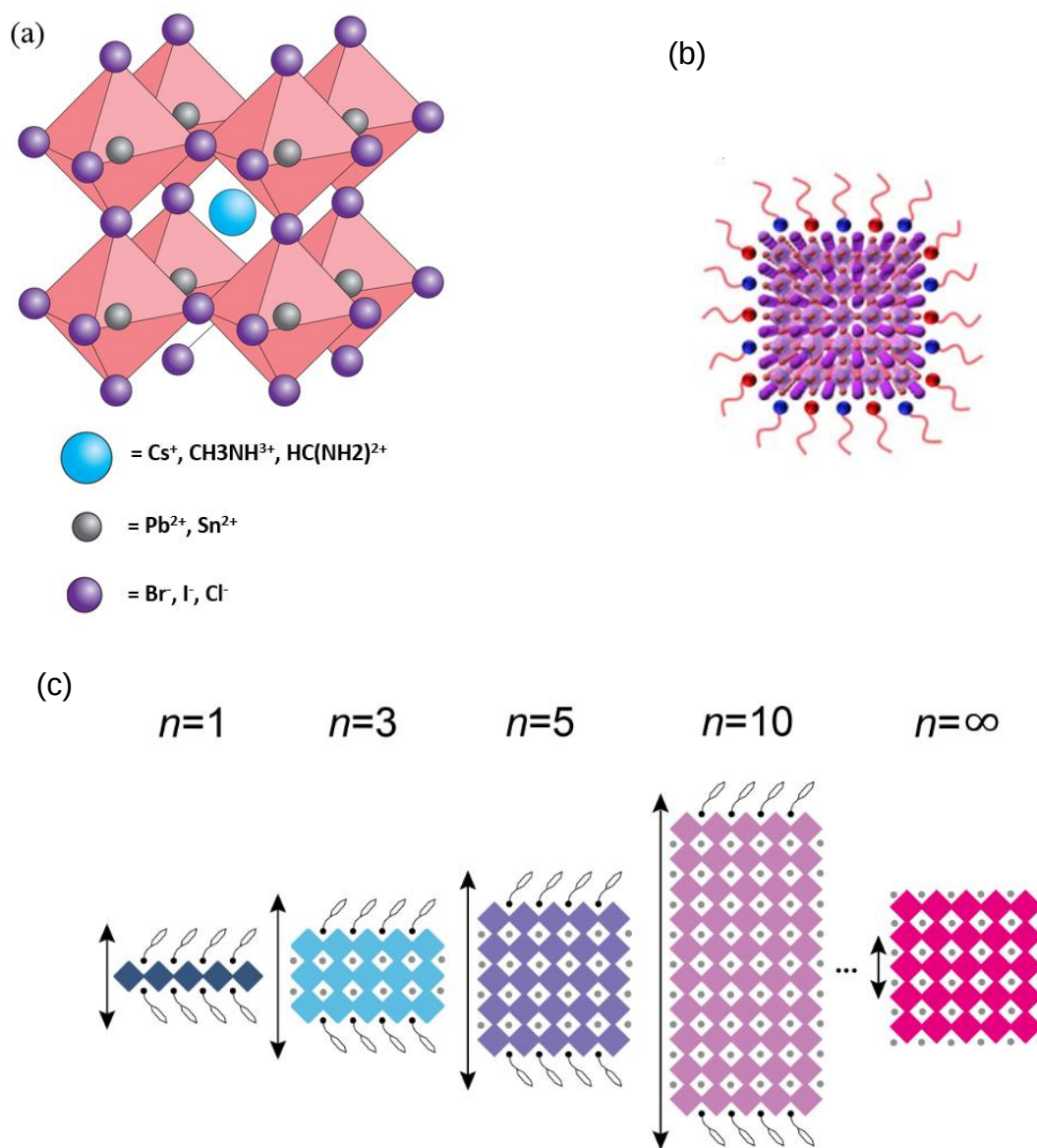


Figure 1- 7 Schematic diagram to show the structure of (a) 3D hybrid perovskite, (b) perovskite quantum dots, (c) layered quasi-2D perovskites.

capped long organic cations, and high radiative recombination rate due to the efficient energy and/or charge transfer through couple 2D domains⁶⁹⁻⁷¹. 0D perovskites such as nanoparticles and quantum dots are emerging as another type of efficient emitter due to their narrow emission spectral width, strong exciton confinement, tunable emission spectrum through size and composition engineering, and high photoluminescence quantum yield (PLQY)⁷²⁻⁷⁴ (**Figure 1-7b**).

1.3.2 Magnetic field effects in metal halide perovskites

In addition to the application in photovoltaic and light emission, magnetic field effects studies on metal halide perovskites have provided in-depth understanding of electronic properties, spin-dependent charge carrier dynamics of perovskites. Theoretical studies showed that the band structure of perovskites is modulated by the strong spin orbital coupling (SOC) from Pb atoms to generate non-degenerate band, $J=3/2$, $J=1/2$ for conduction band and $S=1/2$ for valance band. J-singlet and J-triplet excited states can be generated under photoexcitation or electrical injection⁷⁵. It has been considered that the strong SOC due to heavy elements may significantly shorten spin lifetime in perovskites, and consequently diminishing magnetic field effects. However, in 2015, both Vardeny's group and Hu's group reported that applying a low magnetic field (200mT) can shift the population of electron-hole pairs with different J-states, leading to magnetic field dependent photoluminescence, electro-luminescence, and photovoltaic actions in MHPs at room temperature^{76, 77} (**Figure 1-8a, 1-8b**). The observed magneto-optical phenomena suggest that: 1) a low magnetic field can modify the outcomes of recombination and dissociation process in MHPs by tuning population of J singlet and J triplet, 2) the spin relaxation time in electron-hole pair (or excitons) may be much longer than the free charge carriers in MHPs.

Odenthal *et al.* reported that spin lifetime in excitons of $\text{CH}_3\text{NH}_3\text{PbCl}_{1-x}\text{I}_{3-x}$ may exceed 1ns based on pump-probe Faraday rotation measurement⁷⁸. Recently, a long spin lifetime around 1ns was reported by analyzing the Hanle effect from MAPbBr_3 based spin valve⁷⁹. Both theoretical and experimental studies revealed a long spin lifetime in electron-hole pair states of perovskites which can be comparable to recombination lifetime. The long spin lifetime explains the magneto-optical phenomena observed at room temperature. Also, strong SOC modulated band structure and long spin lifetime suggest a possibility of optically operating spin states by using polarized photoexcitation in MHPs⁸⁰⁻⁸².

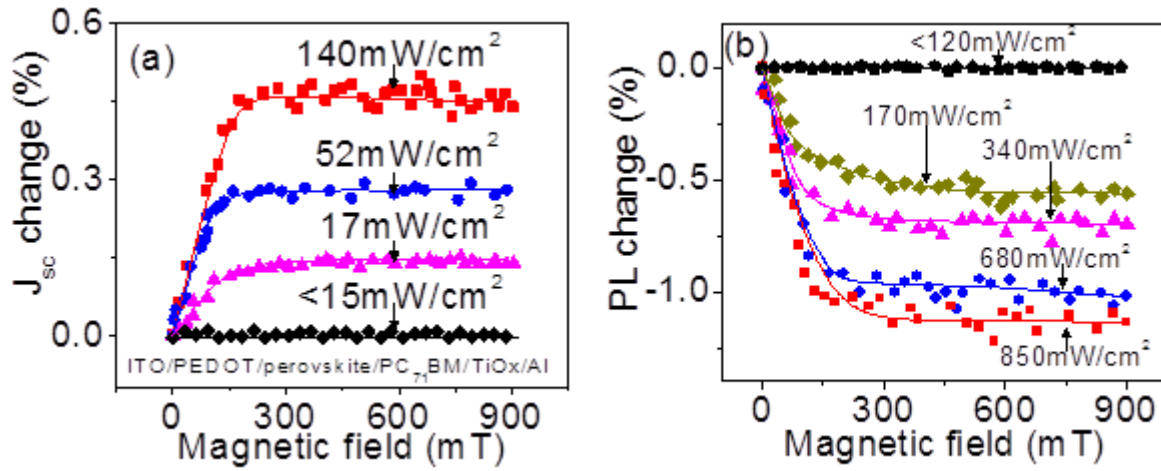


Figure 1- 8 (a) Magneto-photocurrent in the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ solar cell and (b) magneto-photoluminescence in $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ thin film. Data adapted from ref 76.

1.3.3 Rashba effect in metal halide perovskite

Metal halide perovskites exhibit strong spin-orbital coupling due to heavy ions, such as lead, tin, and iodine, in the crystal structure. Inversion symmetry breaking can be found in MHPs due to crystal distortion associated with atomic and orbital displacement^{83, 84}. Rashba effect arises in MHPs when SOC is combined with inversion symmetry breaking in crystal structure. Early theoretical study predicted the existence of Rashba effect in perovskite single crystals. Later on, experimental studies provide further evidence on the presence of Rashba effect in MHPs. Study on circular photo-galvanic effect shows electric current can be generated by oblique incident circular polarized photoexcitation in MHPs thin film⁸⁵. Also, the left-hand and right-hand circular excitation generates electric currents in opposite directions, which provide direct evidence of photo-generated current transport between Rashba spin-split bands. Another experimental study reports that Rashba type band-splitting in MHPs can be tuned based on crystal structure change by applying hydrostatic pressure. It has been shown applying pressure can decrease Rashba splitting, leading to an increase in recombination rate with more direct band recombination⁸⁶.

Rashba effect can have profound influence on the optoelectronic properties of MHPs. Rashba effect can give rise to indirect band nature for MHPs. Charge carriers can be generated in MHPs by light absorption through direct band transition, then go through indirect band transition

with low recombination rate⁸⁷. This may explain the high dissociation rate and long charge carrier lifetime in MHPs solar cells. Nevertheless, Rashba effect can be more prominent in low-dimensional perovskites due to local symmetry breaking at surface⁸⁸. A recent study shows that the band edge exciton fine structure of CsPbBr₃ quantum dots can be strongly affected by Rashba effect and quantum confinement, forming bright triplet states, which can lead to high photoluminescence efficiency in CsPbBr₃ quantum dots⁸⁹. Further understandings on Rashba effect and its influence on charge dissociation and recombination in MHPs are highly demanded.

1.4 Dissertation Outline

The MFEs can be utilized as effective experimental tool to analyze magnetic, electronic and optical properties of multi-functional materials in excited states. However, the study on magneto-optical properties at room temperature with low field in novel multi-functional materials system is still lacking. The fundamental studies on the underlying mechanism of magneto-optical phenomenon are still highly demanded. The research in this thesis mainly focuses on developing unique magneto-optical phenomena in multi-functional materials, such as two-photon absorption based up-conversion crystals, magnetic/semiconducting hybrid 2D nanoparticles, and metal halide perovskites. We will also explore key parameters and processes in determining the magnetic, electronic properties of these multi-functional materials by using various magnetic-optical effects. The outline of this thesis is briefly introduced as follows.

Chapter 2 presents the experimental observation of magnetic field dependent photoluminescence based on multi-photon excitation in rare-earth crystals without magnetic structures. The key parameters that control the observed magneto-photoluminescence, including excitation intensity, exchange interaction, and crystal field are discussed. Chapter 3 reports a unique experimental tool to investigate the dynamic magnetization of nanomaterials under excited states by using magnetic field effect of light scattering. This study also explores a practical method to develop photoexcitation-controllable magnetization through d- π electron coupling in magnetic nanoparticle-graphene 0D-2D hybrid materials. Chapter 4 studies spin and orbit parameters in determining charge recombination and dissociation process in perovskite solar cells. Optically tuning SOC in perovskites is realized by using polarized photoexcitation, and consequently modifying photovoltaic actions. Chapter 5 explores the dipole moment effect on light emission efficiency in perovskite nanoparticles through cation doping. This work shows that the SOC

associated with electric polarization in perovskite nanoparticles can be influenced by substituting organic cation with a lower dipole moment. Chapter 6 presents a summary of the studies in this thesis and the outlook for future works.

Chapter 2 Magneto-photoluminescence based on Two-photon Excitation in Lanthanide Doped Up-conversion Crystals

2.1 Abstract

This chapter is mainly focused on experimental studies on magneto-photoluminescence based on two-photon excitation in up-conversion $\text{Y}_2\text{O}_3\text{S: Er, Yb}$ crystal particles. We find that the up-conversion photoluminescence generated by two-photon excitation exhibits magnetic field effects at room temperature, leading to a two-photon excitation induced magneto-photoluminescence when the two-photon excitation exceeds the critical intensity. By considering the spin selection rule in electronic transitions, we propose that spin-antiparallel and spin-parallel transition dipoles with spin-mixing are accountable for the observed magneto-photoluminescence. Specifically, the two-photon excitation generates spin-antiparallel electric dipoles between $4\text{S}^{3/2}-4\text{I}^{15/2}$ in Er^{3+} ions. The antiparallel spins are conserved by exchange interaction within dipoles. When the photoexcitation exceeds the critical intensity, the Coulomb screening can decrease the exchange interaction. Consequently, the spin-orbital coupling can partially convert the antiparallel dipoles into parallel dipoles, generating a spin mixing. Eventually, the populations between antiparallel and parallel dipoles reach an equilibrium established by the competition between exchange interaction and spin-orbital coupling. Applying a magnetic field can break the equilibrium by disturbing spin-mixing through introducing spin precessions, changing the spin populations on antiparallel and parallel dipoles and leading to the magneto-photoluminescence. Therefore, spin-dependent transition dipoles present a convenient mechanism to realize magneto-photoluminescence in multi-photon up-conversion crystal particles.

2.2 Introduction

Magneto-photoluminescence is a typical phenomenon in magnetic field effects (MFE) of excited states in excitonic light-emitting materials^{21, 90, 91}. In excitonic light-emitting materials, the excited states become spin dependent to form singlet and triplet states. When a magnetic field changes the singlet and triplet populations, magnetic field effects can be observed in excited states because the singlets and triplets generate different optical and electrical outcomes. As a result, excitonic materials have demonstrated magnetic field effects of photoluminescence⁹¹, photocurrent^{15, 92, 93}, electroluminescence⁹⁴⁻⁹⁶, electrical current^{16, 20, 97}, and electrical polarization^{25, 98}. Clearly, spin-dependent excited states become a necessary condition to develop magnetic field effects in excitonic materials. However, it remains as an un-addressed issue on whether non-excitonic materials can demonstrate magnetic field effects in excited states. Here, we select up-

converting rare-earth light-emitting crystal particles, as an example for non-excitonic materials, to explore the possibilities of realizing magneto-photoluminescence by considering spin-dependent transition dipoles. Specifically, we consider that an incident photon can generate a transition dipole with antiparallel spins, due to spin selection rule, formed between an excited electron and ionic core. On the other hand, the heavy lanthanide elements can provide a strong spin-orbital coupling (SOC) that can partially convert the spin-antiparallel dipoles into spin-parallel dipoles through spin flipping mechanism, leading to a spin mixing. We should note that an exchange interaction can be established based on the electrostatic Coulomb interaction within transition dipole. This exchange interaction intends to conserve the spin-antiparallel dipoles, against the spin mixing generated by SOC. We can expect that the competition between the exchange interaction and SOC leads to an equilibrium on the populations of spin-antiparallel and spin-parallel dipoles. If a magnetic field can disturb the equilibrium established by the competition between exchange interaction and SOC, the populations of spin-antiparallel and spin-parallel dipoles can be modified, changing photoluminescence intensity and leading to a magneto-photoluminescence. Therefore, spin-dependent transition dipoles can present a convenient mechanism to realize magneto-photoluminescence in non-excitonic light-emitting materials.

2.3 Materials and Methods

2.3.1 Sample preparation and characterization

The X-ray powder diffraction was performed on Bruker AXS D2 diffractometer using Cu-K α radiation. The size and morphology of Y₂O₂S: Er, Yb were characterized by Hitachi TM3030 scanning electron microscope. The Y₂O₂S: Er, Yb films were fabricated by drop-casting Y₂O₂S: Er, Yb suspension solutions (2mg/mL Y₂O₂S: Er, Yb and 10mg/mL Poly (methyl methacrylate) (PMMA) in chloroform) on quartz substrates. NaYF₄: Er, Yb, and NaYF₄: Tm, Yb thin films were fabricated with the same method.

2.3.2 Magneto-photoluminescence measurement

The magneto-photoluminescence measurements were performed by using SPEX fluorolog 3 spectrometer combined with an electrically controllable magnet. The photoexcitations were provided from 980nm and 325nm CW laser beams for up-conversion and down-conversion

photoluminescence, respectively. The photoluminescence emission is collected by an optical fiber and directed to the spectrometer (**Figure 2-1**). The MFE_{PL} magnitude is defined as $MFE = (I_B - I_0)/I_0$, where I_B and I_0 represent the photoluminescence intensities in the situations with and without magnetic field, respectively.

2.4 Results and Discussion

Figure 2-2a shows the X-ray diffraction patterns of $Y_2O_2S: Er, Yb$ powder. The peak position and intensity agree well with standard Y_2O_2S hexagonal phase. The SEM image in **Figure 2-2b** reveals that the particle size ranges from hundreds of nanometers to several microns. **Figure 2-2c** shows the up-conversion light-emitting spectrum of $Y_2O_2S: Er, Yb$ particles under 980nm continuous-wave laser excitation at different intensities. We can see that two emission peaks at 528nm and 551nm correspond to $^2H_{11/2} - ^4I_{15/2}$ and $^4S_{3/2} - ^4I_{15/2}$ transitions of the doped Er^{3+} ions, respectively⁹⁹. The emission-excitation intensity dependence in **Figure 2-2d** confirms the two-photon up-conversion light emission based on the curve slop of 1.9. In the Er, Yb co-doped system, the green up-conversion emission is realized through two consecutive steps: (i) the electrons are excited to the $^4I_{11/2}$ of Er^{3+} ion via energy transfer from neighboring excited Yb^{3+} ion under first photon excitation and (ii) excited electrons at the $^4I_{11/2}$ is further excited to $^4F_{7/2}$ level by either energy transfer from excited Yb^{3+} ion or excited state absorption under second photon excitation. The $^2H_{11/2}$ and $^4S_{3/2}$ are then populated by the subsequent multi-phonon relaxation of $^4F_{7/2} - ^2H_{11/2}$ and $^4F_{7/2} - ^4S_{3/2}$ towards up-conversion emission via $^2H_{11/2} - ^4I_{15/2}$, $^4S_{3/2} - ^4I_{15/2}$.

It is interesting to note in **Figure 2-3a** that a magneto-photoluminescence can be observed in the $Y_2O_2S: Er, Yb$ particles under two-photon excitation of 980 nm laser beam when the excitation exceeds the critical intensity of 2080mW/cm². Here, the magneto-photoluminescence amplitude is defined as: $MFE = (I_B - I_0)/I_0$, where I_B and I_0 are the photoluminescence intensities with and without external magnetic field. In this two-photon induced magneto-photoluminescence, the up-conversion light emission intensity gradually increases with the magnetic field up to around 300 mT and becomes saturated with further increasing magnetic field. The magneto-photoluminescence shows a typical Lorentzian line-shape with an amplitude of 2.1% at the excitation intensity of 4680 mW/cm² of 980 nm laser beam. We should point out that, below the

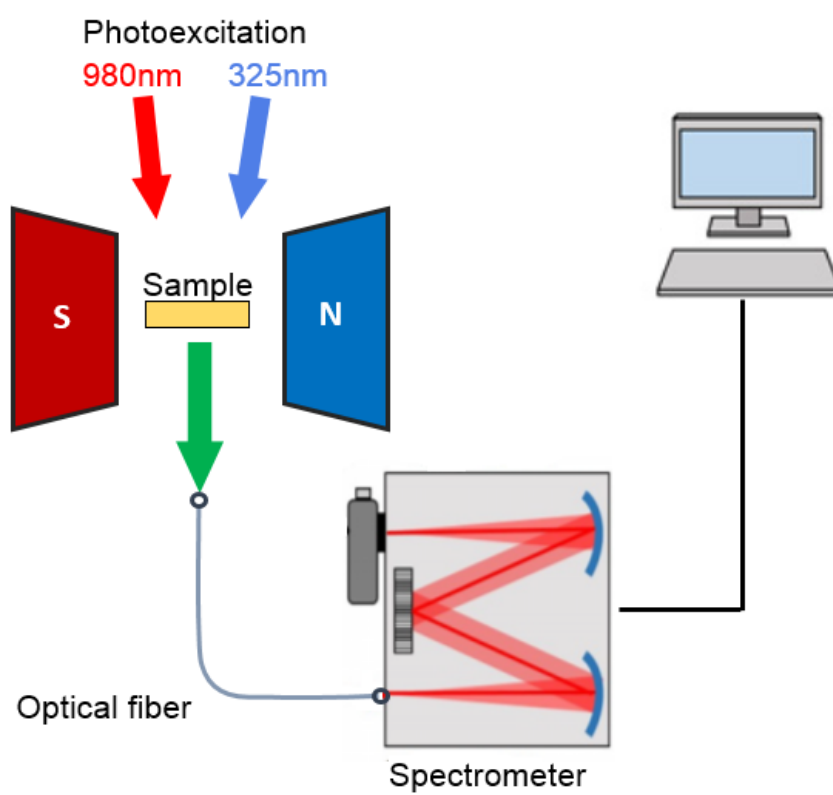


Figure 2- 1 Measurement setup for magneto-photoluminescence.

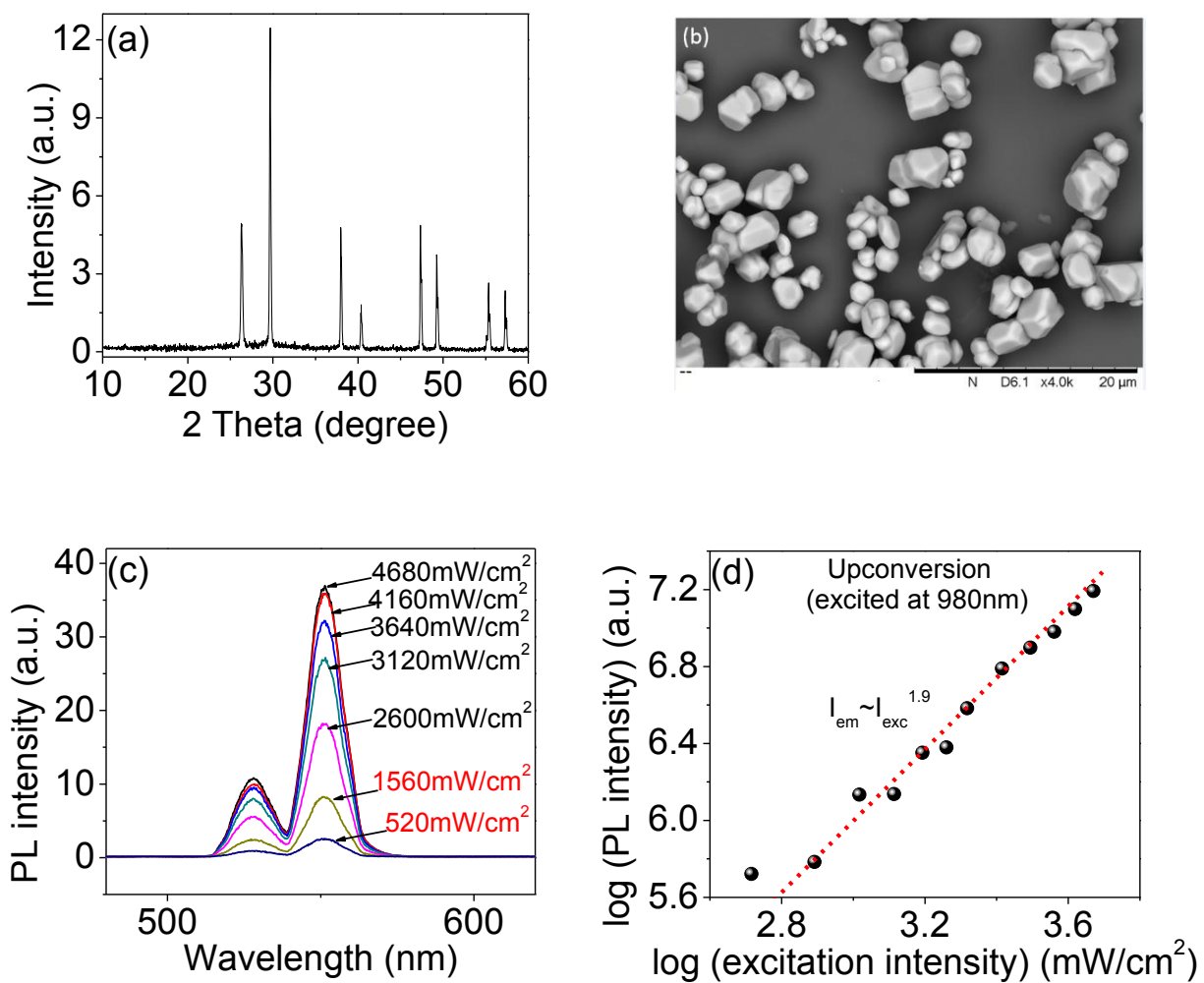


Figure 2- 2 (a) X-ray powder diffraction patterns of Y₂O₂S: Er, Yb. (b) SEM image of Y₂O₂S: Er, Yb particles. (c) Up-conversion luminescence spectrum under different intensities 980nm IR laser excitation. (d) up-conversion emission intensity as a function of excitation intensity.

critical excitation intensity (2080mW/cm^2), the magneto-photoluminescence becomes negligible, although the up-conversion emission is still very strong (**Figure 2-2c**).

To understand the two-photon induced magneto-photoluminescence, we consider that an excited electron forms an electric transition dipole with the ionic core in lanthanide-doped up-converting materials. We should note that the spin selection rule only allows the transition dipoles to be generated with antiparallel spins. Within the lifetime of transition dipoles, there are two competing parameters: exchange interaction and spin-orbital coupling that intend to conserve and change the antiparallel spins in transition dipoles generated by two-photon excitation, leading to spin-conserving and spin-mixing processes, respectively. If the exchange interaction is strong through the Coulomb interaction within transition dipoles, magneto-photoluminescence can be negligible, as demonstrated in Frenkel excitons¹⁰⁰⁻¹⁰². In this situation, a strong exchange interaction can conserve the antiparallel spins in transition dipoles, dis-allowing spin mixing to occur. And a magnetic field is not able to compete with the strong exchange interaction, leading to negligible magneto-photoluminescence, although the transition dipoles still generate photoluminescence through radiative recombination under two-photon excitation. Here, we suggest that increasing excitation intensity can cause a Coulomb screening between transition dipoles and consequently decreases the exchange interaction within transition dipoles. As the excitation intensity is gradually increased, the exchange interaction can be lowered to a value similar to spin-orbital coupling. In this case, the spin-antiparallel dipoles can be partially converted into spin-parallel dipoles through spin flipping caused by spin-orbital coupling, leading to a spin mixing from spin-antiparallel to spin-parallel dipoles. The competition between exchange interaction and spin-orbital coupling reaches an equilibrium on the populations between antiparallel and parallel dipoles. Based on the theories of magnetic field effects^{76, 103, 104}, applying a magnetic field can disturb the equilibrium on the populations between antiparallel and parallel dipoles by introducing coherent spin precessions, leading to enhancement in spin conservation and decrease in spin mixing. As a consequence, positive magneto-photoluminescence can be observed due to the increased population of antiparallel transition dipoles under magnetic field. This analysis indicates that tuning two-photon excitation intensity can activate the spin-mixing between antiparallel and parallel transition dipoles, consequently generating a two-photon induced magneto-photoluminescence in up-conversion light-emitting materials.

To further study the magneto-photoluminescence observed from $\text{Y}_2\text{O}_2\text{S: Er, Yb}$ particles, we explore magneto-photoluminescence under down-conversion light emission through one-photon excitation of 325nm laser beam. We can see in **Figure 2-3b** that a down-conversion magneto-photoluminescence can be observed when the one-photon excitation exceeds the intensity of 500 mW/cm^2 of 325 nm CW laser beam. The down-conversion magneto-photoluminescence shows a broader line-shape with non-Lorentzian characteristics. The broader line-shape implies that the down conversion through one-photon excitation corresponds to a stronger exchange interaction within transition dipoles, as compared to up conversion through two-photon excitation. In particular, this can suggest that the one-photon and two-photon excitations can cause weaker and stronger electrical polarizations, and consequently affects the Coulomb screening effect of exchange interaction. In down-conversion, the magneto-photoluminescence amplitude gradually increases with magnetic field up to 600 mT and becomes saturated with further increasing magnetic field. In addition, the down-conversion emission spectrum is almost identical to the up-conversion emission spectrum which is composed of two peaks at 528nm and 554nm corresponding to $^2\text{H}_{11/2}$ - $^4\text{I}_{15/2}$ and $^4\text{S}_{3/2}$ - $^4\text{I}_{15/2}$ transitions of the Er^{3+} ions (**Figure 2-3c**). **Figure 2-3d** shows the emission-excitation intensity dependence under down-conversion to indicate the one-photon excitation process. Clearly, the one-photon excitation based magneto-photoluminescence supports the proposed mechanism for two-photon excitation based magneto-photoluminescence: spin-dependent transition dipoles associated with $^4\text{S}_{3/2}$ - $^4\text{I}_{15/2}$ transitions are accountable for up-conversion magneto-photoluminescence based on excitation intensity-controllable spin-mixing in the $\text{Y}_2\text{O}_2\text{S: Er, Yb}$ particles.

To simplify the discussion of magneto-photoluminescence in up-conversion luminescence (UCL), we consider a three-level system, namely ground state, intermediate level, and upper level, in up-conversion particles. The up-conversion is realized by two consecutive excitations from the ground state to the intermediate level and upper level (**Figure 2-4**). According to theoretical calculation, at low excitation intensities the excited electrons in intermediate level are mainly consumed by linear decay to ground states^{105, 106}, leading to a much lower population in up-conversion luminescence level compared with intermediate level. In this situation, the transition dipoles are formed between the ground state and up-conversion luminescence. The negligible magneto-photoluminescence implies that the transition dipoles possess a strong exchange interaction at low excitation intensities. However, at high excitation intensities, the dominated

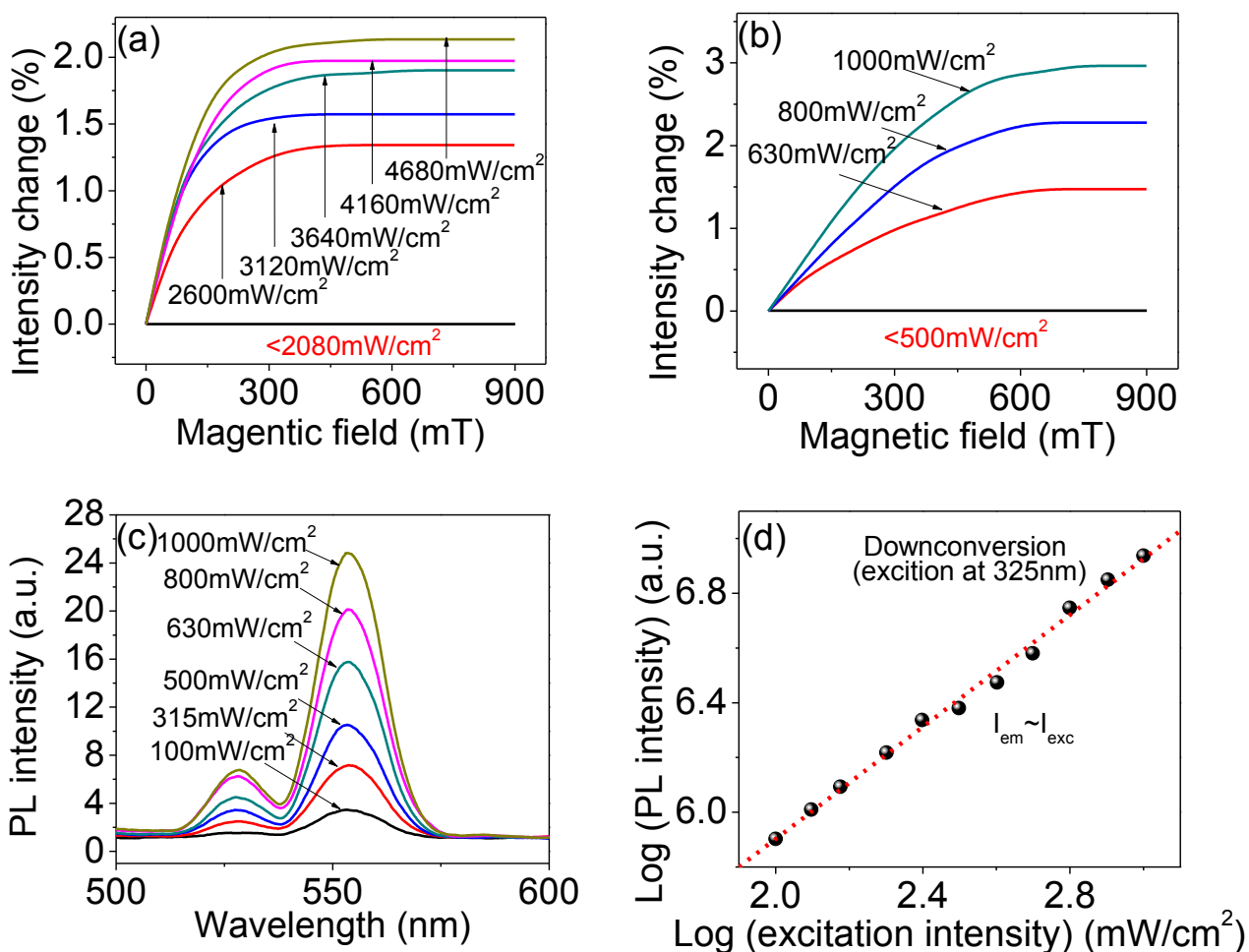


Figure 2- 3 (a) Magneto-photoluminescence of $\text{Y}_2\text{O}_2\text{S: Er, Yb}$ under high intensity 980nm IR laser excitation. (b) Magneto-photoluminescence of $\text{Y}_2\text{O}_2\text{S: Er, Yb}$ under high intensity 325nm laser excitation. (c) Down-conversion luminescence spectrum under different intensities 325nm laser excitation. (d) Down-conversion emission intensity as a function of excitation intensity.

depletion mechanism of excited electrons at intermediate level becomes up-conversion, which leads to a large population in the up-conversion luminescence level. The appreciable magneto-photoluminescence suggests that the electric dipoles can be formed with weak exchange interaction at high excitation intensities. Normally, when the exchange interaction is within micro eV, the SOC can cause a spin mixing, leading to coexisted spin antiparallel and parallel electric dipoles. Applying a magnetic field (< 1 Tesla) can decrease the spin mixing by introducing coherent spin precessions and thus modify the populations of antiparallel and parallel electric dipoles, generating a positive magneto-photoluminescence. We should point out that electric dipoles can be also formed at the intermediate level. By considering that strong up-conversion photoluminescence still occurs below the critical intensity (2080 mW/cm^2) required for magneto-photoluminescence (**Figures 2-2c and 2-3c**), we suggest that the transition dipoles at up-conversion luminescence level are accountable for the observed magneto-photoluminescence. Therefore, the spin-dependent electric dipoles together with operative spin mixing at up-conversion luminescence level becomes a necessary condition to realize magneto-photoluminescence in up-conversion particles.

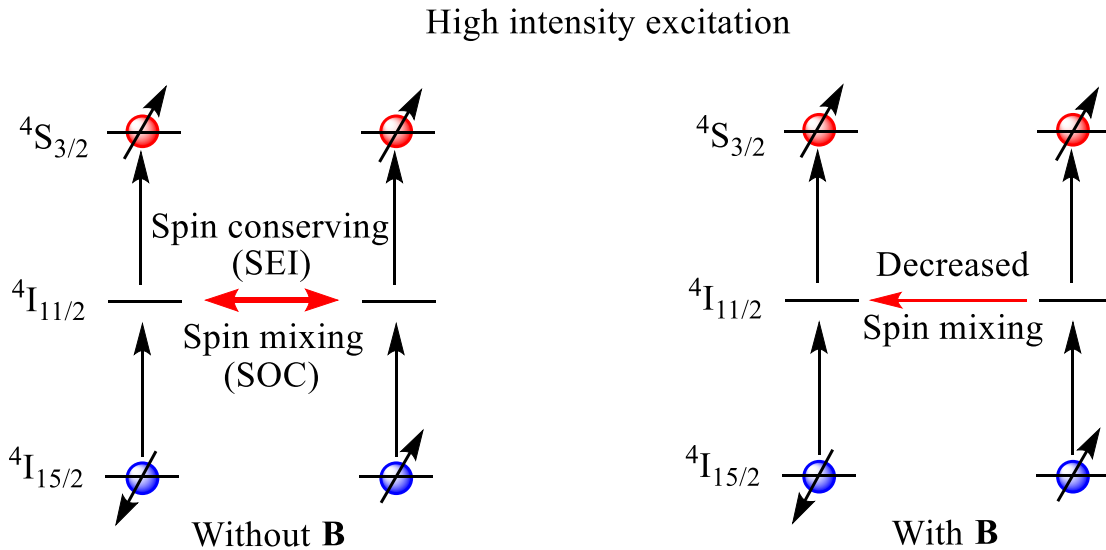


Figure 2- 4 Magneto-photoluminescence generation in two photon up-conversion process by magnetically disturbing the balance of population of transition dipoles with different spin states.

We can see in **Figure 2-5a** that the up-converting NaYF₄: Er, Yb exhibits negligible magneto-photoluminescence at the intensity of 4680 mW/cm² under two-photon excitation of 980 nm laser beam. This indicates that a magnetic field can hardly change the populations of spin-antiparallel and spin-parallel dipoles. This negligible magneto-photoluminescence can be caused by two different possibilities. First, the spin lifetime becomes shorter than the photoluminescence. In this case, introducing coherent spin precessions upon applying a magnetic field cannot change the populations of spin-antiparallel and spin-parallel dipoles. Second, the exchange interaction becomes strong, disallowing any spin mixing and leading to un-changed spin populations on transition dipoles. We should note that, because of the same lanthanide ions, the Y₂O₂S: Er, Yb and the NaYF₄: Er, Yb can have similar SOC controlled by Er³⁺ and Yb³⁺ ions. Therefore, the negligible magneto-photoluminescence implies that the Y₂O₂S: Er, Yb possesses a strong exchange interaction which disallows the spin mixing. Here, we consider the effects of crystal field on the exchange interaction. Specifically, the host crystal lattice can exert crystal field on the dopant RE ions which substitute the cation sites of the host lattice due to the ion size mismatch¹⁰⁷⁻¹⁰⁹. The crystal field can also be affected by morphology and crystallinity of the crystals^{110, 111}. In this light, the Er³⁺ and Yb³⁺ ions in NaYF₄ host crystals can be subjected to different crystal fields as compared to Y₂O₂S host crystals, leading to an enhanced spin-exchange interaction with the consequence of negligible magneto-photoluminescence. Nevertheless, this phenomenon suggests that changing the exchange interaction can largely affect the magneto-photoluminescence in up-converting rare-earth light-emitting materials.

Figure 2-5b shows the normalized magneto-photoluminescence generated by up-conversion and down-conversion under 325 nm (630 mW/cm²) and 980 nm (2600 mW/cm²) excitations in the Y₂O₂S: Er, Yb particles. In comparison with up-conversion magneto-photoluminescence, the down-conversion magneto-photoluminescence exhibits a broader line-shape characteristic, indicating a stronger exchange interaction. We should point out that the up-conversion and down-conversion show much stronger and weaker light emission, respectively, at the critical intensity (2080 mW/cm² for 980 nm laser) and (500 mW/cm² for 325 nm) required to generate magneto-photoluminescence. This phenomenon means that, at the condition of generating magneto-photoluminescence, the up-conversion and down-conversion correspond to higher and lower densities of electrical dipoles at UCL level. In particular, increasing the density of electric dipoles can weaken the Coulomb attraction within the electric dipoles due to Coulomb

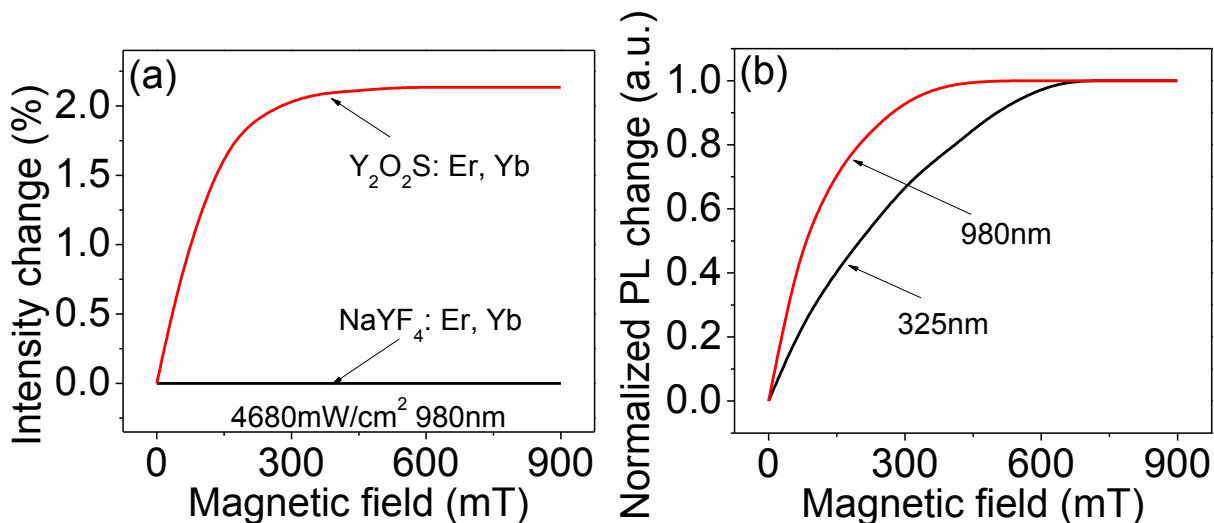


Figure 2- 5 (a) Magneto-photoluminescence of $Y_2O_2S: Er, Yb$ and $NaYF_4: Er, Yb$ under high intensity 980nm IR laser excitation. (b) Normalized magneto-photoluminescence characteristics under 325nm and 980nm photoexcitation.

screening effect and thus decreases the exchange interaction^{98, 112}. As a consequence, the up-conversion and down-conversion can lead to narrow and broader line-shape characteristics in magneto-photoluminescence.

We further study magneto-photoluminescence through three photon process in the $NaYF_4: Tm, Yb$ particles. **Figure 2-6a** shows up-conversion emission under 980 nm laser excitation with different intensities. Two emission peaks are obtained at 450 nm and 475 nm corresponding to $^1D_2-^3H_5$ and $^1G_4-^3H_6$ transitions, respectively. The photoluminescence-excitation intensity dependence with the slope of 2.4 confirms that the blue emission in Tm and Yb co-doped system is a three photon process. **Figure 2-6b** shows that magneto-photoluminescence can be observed when the 980 nm excitation exceeds the critical intensity of 3120 mW/cm², similar to the phenomenon observed in the two-photon process in the Er, Yb co-doped system. Here, we note that the three-photon system ($NaYF_4: Tm, Yb$) exhibits a much broader line-shape in magneto-photoluminescence comparing with the two-photon system ($Y_2O_2S: Er, Yb$) (**Figure 2-6c**). The broader line-shape in magneto-photoluminescence implies that the populations on spin-antiparallel

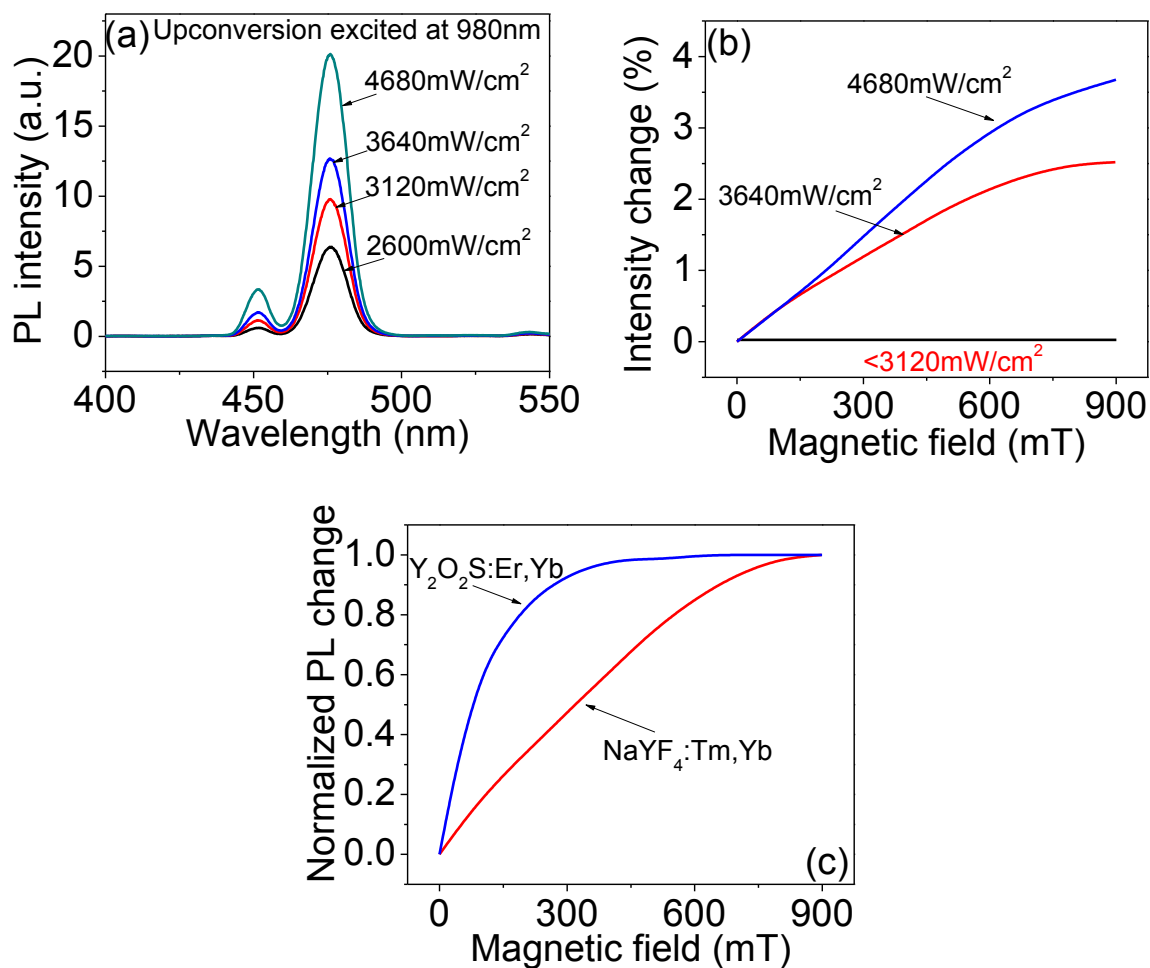


Figure 2- 6 (a) Up-conversion luminescence spectrum of NaYF₄: Tm, Yb under different intensities 980nm IR laser excitation. (b) Magneto-photoluminescence of NaYF₄: Tm, Yb under high intensity excitation. (c) Normalized magneto-photoluminescence of different up-converting materials under 3640mW/cm² 980nm photoexcitation.

and spin-parallel dipoles are more difficult to disturb in the NaYF₄: Tm, Yb upon applying a magnetic field. Based on the fact that the NaYF₄: Tm, Yb has a similar SOC due to the same heavy lanthanide elements as compared to the Y₂O₂S: Er, Yb, the broader line-shape can suggest that the NaYF₄: Tm, Yb exhibits a stronger exchange interaction under three-photon excitation.

2.5 Summary

This chapter reports experimentally study on up-conversion magneto-photoluminescence by using two-photon and three-photon excitations based on the Y₂O₂S: Er, Yb and NaYF₄: Tm, Yb particles. We found that magneto-photoluminescence can be observed when the excitation exceeds the critical intensity in both two-photon and three-photon processes. We proposed that spin-dependent transition dipoles with operative spin mixing between antiparallel and parallel spins form the necessary condition to generate magneto-photoluminescence in up-conversion materials. Specifically, the electric dipoles can be formed initially with antiparallel spins through electronic transitions between ground state and up-conversion level based on spin selection rule. When the excitation exceeds the critical intensity, the exchange interaction within electric dipoles becomes weak reaching μeV , allowing spin mixing to occur under the influence of SOC, and partially converting the antiparallel electric dipoles into parallel electric dipoles. The populations of antiparallel and parallel dipoles reach equilibrium due to the competition between the spin mixing from SOC and the spin conserving from exchange interaction in up-conversion materials. An external magnetic field can then disturb the equilibrium established by the competition between spin mixing and spin conserving, modifying the populations on antiparallel and parallel dipoles. This leads to a magneto-photoluminescence through up-conversion when the electric dipoles undergo radiative emission. By comparing the magneto-photoluminescence from the up-conversion particles with different host materials, we find that the exchange interaction between the electron and ionic core is the critical parameter in determining the magneto-photoluminescence in up-conversion particles. Therefore, our experimental studies provide new insight to generate magneto-optical effects in up-conversion materials by considering the spin-dependent electric dipoles together with operative spin mixing between antiparallel and parallel spins.

Chapter 3 Photoexcitation-controllable Magnetization in γ -Fe₂O₃-Graphene (0D-2D) Nanohybrids

3.1 Abstract

This chapter presents photoexcitation-enhanced magnetization in $\gamma\text{Fe}_2\text{O}_3$ -Graphene (0D-2D) van der Waals heterostructures based on the experimental studies of steady-state pump-probe measurements. It is observed that applying a magnetic field on the $\gamma\text{-Fe}_2\text{O}_3$ /graphene material suspended in an organic solvent can cause a light scattering on the probe beam in the absence of pump beam, leading to a magnetic field effect of light scattering. This result shows that the magnetization on the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles can lead to a partial orientation of Fe_2O_3 -graphene heterostructure components suspended in liquid. This effect of magnetic field on light scattering is caused by the dynamic magnetization of the superparamagnetic-semiconducting hybrid material. Interestingly, applying the pump beam functioning as photoexcitation can lead to an enhancement on the scattering of probe beam, increasing magnetic field effect of light scattering. The increased magnetic field effect of light scattering indicates that the photoexcitation from the pump beam applied to the hybrid enhances the magnetization on the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles through the d- π electron coupling between $\gamma\text{-Fe}_2\text{O}_3$ and graphene in the hybrid material. This d- π electron coupling can be a practical method to develop photoexcitation-controllable magnetization through excited states based on chemically linked magnetic-semiconducting hybrid design.

3.2 Introduction

Photoexcitation-controllable magnetization offers unique principles for developing magneto-optical properties. Generally, semiconducting materials can exhibit significant response in charge transport and electric polarization under photoexcitation¹¹³⁻¹¹⁶, while magnetic nanoparticles can be magnetized by applying an external magnetic field due to the localized spins^{117, 118}. Incorporating magnetic nanoparticles into semiconducting materials in well-balanced systems provides a possible method to realize optical tuning on magnetic properties through the internal coupling between excited states in semiconductors and local spins in magnetic nanoparticles. In this work, we explore the possibilities of realizing the photoexcitation-controllable magnetization by chemically linking the magnetic $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles and 2-D graphene based on the experimental studies of pump-probe measurements in the magnetic field. The $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles are well-known magnetic nanoparticles with size-dependent magnetization and coercivity¹¹⁹⁻¹²¹. In particular, the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles allow the surface modification by using organic ligands, ready for chemically integrating with semiconducting

materials towards the development of magneto-optical effects. On the other hand, the 2-D semiconducting graphene possesses highly anisotropic optic and magnetic properties^{26, 122-130} due to the coexisted delocalized and localized π electrons¹²²⁻¹²⁵. Here, the semiconducting graphene is chemically linked with magnetic γ -Fe₂O₃ particles by using organic π -conjugated structures to form magnetic-semiconducting hybrid materials. The pump-probe measurements in magnetic field are applied to the magnetic-semiconducting γ -Fe₂O₃/graphene hybrid materials suspended in organic solvent to explore photoexcitation-controllable magnetization. Specifically, the pump beam functions as a photoexcitation to generate excited states in the semiconducting graphene. When the suspended γ -Fe₂O₃/graphene hybrid material is placed in a magnetic field, the probe beam can be scattered by the semiconducting graphene upon magnetization-induced orientation. Therefore, the pump-probe measurement leads to magnetic field effects of light-scattering in excited states to explore the photoexcitation-controllable magnetization based on magnetic-semiconducting γ -Fe₂O₃/graphene hybrid materials. By using the pump-probe measurements in magnetic field, we find that the magnetization in the γ -Fe₂O₃ nanoparticles can be increased by applying a photoexcitation through excited states in semiconducting graphene in the γ -Fe₂O₃-graphene hybrid material.

3.3 Materials and Methods

3.3.1 Materials synthesis

For γ -Fe₂O₃ functionalized graphene nanohybrid, the monolayer graphene is prepared by standard electrochemical exfoliation method using platinum as the counter electrode and a graphite flake as the working electrode¹³¹. The γ -Fe₂O₃ nanoparticles are functionalized with the ligand Y and coupled with graphene in *N*-methyl pyrrolidone (NMP) solvent at room temperature through self-assembly (**Figure 3-1a**). Then the γ -Fe₂O₃ graphene nanohybrids are dispersed into NMP to form suspension with concentration of 2mg/ml for light scattering measurement.

3.3.2 Magnetic field effect of light scattering measurement

For light scattering measurement, the γ -Fe₂O₃ graphene nanohybrids (structure illustrated as **Figure 3-1a**) were dispersed into NMP to form suspension with concentration of 2mg/ml. The suspension was sealed in a quartz vial placed in a magnetic field generated by an electrical magnet.

The incident beam was provided from a YAG solid-state laser at 532 nm with an output intensity of 8 mW/cm². The scattered light was collected by an optical fiber and measured by SPEX Fluorolog-3 spectrometer. For the MFE of light scattering measurement under excited state, pump beam from a He-Cd laser at 325 nm was used to excite the suspended nanohybrid (**Figure 3-1b**).

3.4 Results and Discussion

We have carried out experimental measurements on the transmission electron microscopy (TEM) images for γ -Fe₂O₃-graphene hybrid material (MYG), as shown in **Figure 3-2a**. The MYG nanohybrid was synthesized by coupling γ -Fe₂O₃ with electrochemically exfoliated graphene with aid of a ligand Y. The ligand Y has a catechol residue with two hydroxyl groups at one end and a pyrene moiety at the other terminal, as given in the inset of **Figure 3-2a**. The catechol residue binds with the surface of the nanoparticle while the pyrene residue interacts with the surface of graphene through van der Waals interactions. The average size of the graphene flakes used to synthesize MYG is 1-3 microns. The nanoparticles were separately functionalized with the ligand Y and combined with graphene in *N*-methyl pyrrolidone (NMP) solvent at room temperature. The MYG nanohybrid is formed by the spontaneous self-assembly of the functionalized γ -Fe₂O₃ onto graphene in NMP solution. Since the MYG nanohybrid of γ -Fe₂O₃ and graphene are assembled by van der Waals forces between the pyrene group in ligand Y and the surface of graphene, the MYG nanohybrid can be considered a zero dimensional-two dimensional (0D-2D) van der Waals

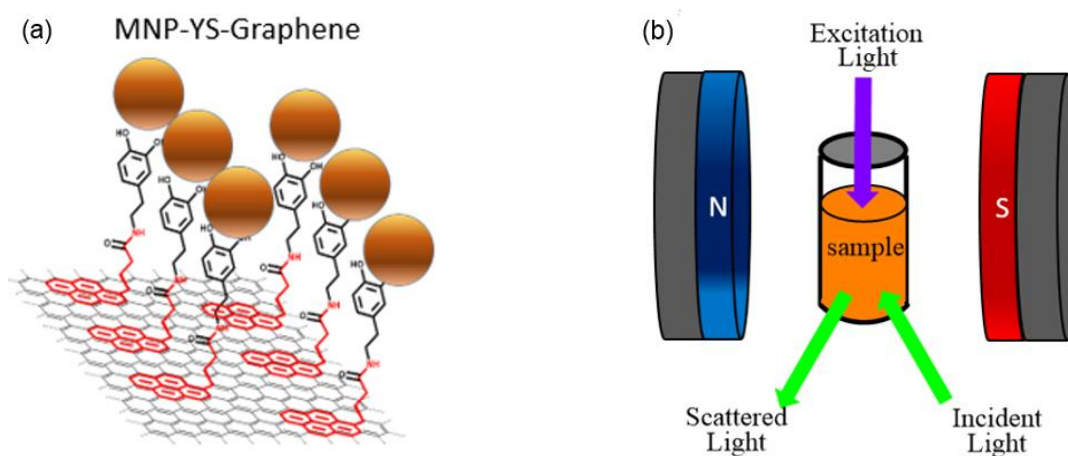


Figure 3- 1 (a) Schematic of self-assembled MYG nanohybrid. (b) Measurement setup of magnetic field effect of light scattering.

heterostructure¹³²⁻¹³⁴. The schematic of the setup for the magnetic field effect of light scattering (MFE_{LS}) measurement can be seen in **Figure 3-2b**, the suspension is sealed in a quartz vial placed in a magnetic field generated by an electrical magnet. A 532 nm continuous-wave laser is used as probe beam to generate scattered light in magnetic field, and a 325 nm continuous-wave laser is used as pump beam to generate excited states in both graphene and magnetic nanoparticles. The magnetic field is linearly increased for the MFE_{LS} measurement. It is kept constant at a given magnetic field strength during the time dependent measurement for analysis of magnetic torque generation under magnetic field. Absorption spectrum in **Figure 3-2c** reveals that MYG, graphene and the ligand Y have strong absorption below 400nm wavelength, which indicates that excited states can be generated within all these three components under 325nm laser excitation. The presence of characteristic pyrene peaks at 327 nm and 343 nm MYG is further evidence of the coupling of γ -Fe₂O₃ on to graphene.

The ground state MFE_{LS} signal from MYG nanohybrid can be seen in **Figure 3-3a**. The amplitude of MFE_{LS} is defined as: $MFE = (I_B - I_0)/I_0$, where I_B and I_0 are the scattered light intensities with and without external magnetic field. The light scattering intensity collected in the out of plane direction can be seen gradually increasing with applied magnetic field in **Figure 3-3a**. The scattering intensity gradually increases with the applied magnetic field and saturates at the MFE_{LS} amplitude of 12.4% for MYG. The enhancement in light scattering intensities is an indication that the MYG particles can be orientated parallel to the in-plane direction of magnetic field leading to larger reflection surface under magnetic field. The orientation of suspended particles can be determined by the magnetic energy generated by magnetic polarization, as shown in Eq. (1)¹²³

$$\langle \cos^2 \theta \rangle = C \cdot \frac{\Delta\chi V H^2}{kT} \quad (3-1)$$

where θ is the angle between spin polarization and magnetizing field H , $\Delta\chi$ is the difference between the magnetic susceptibilities along different directions, V is the average volume of individual nanoparticles, C is the constant. The MFE_{LS} results are clear evidence to show anisotropic magnetization in the suspended MYG particles upon applying a magnetic field. The time-dependent MFE_{LS} results measured under fixed magnetic field strength are given in **Figure 3-3b**. It can be seen that a higher MFE_{LS} amplitude can be generated under higher magnetic field. Under 450mT and 900mT magnetic field, MYG shows MFE_{LS} with the amplitude of 12.1% and

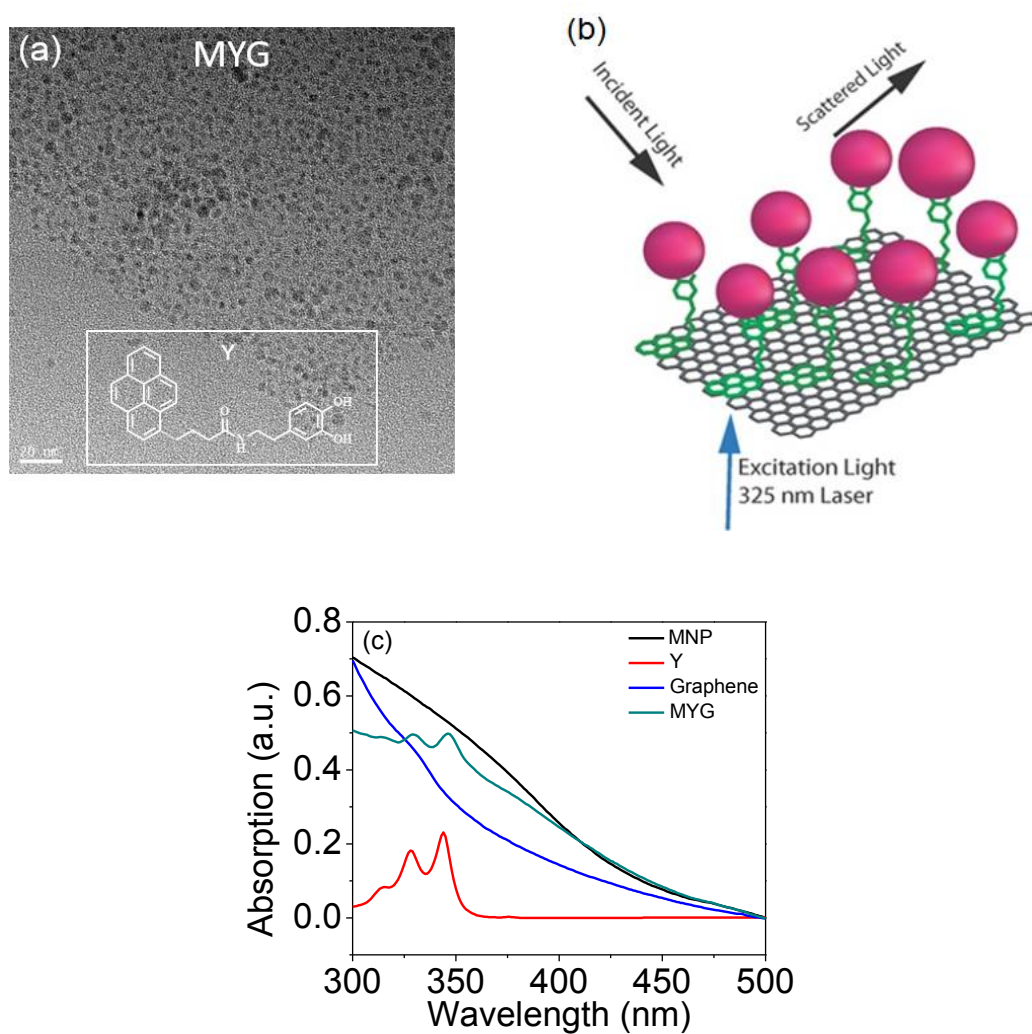


Figure 3- 2 (a) TEM image to show the morphology of magnetic nanoparticle functionalized graphene (MYG). The inset shows the chemical structure of ligand Y. (b) Schematic setup for measuring magnetic field effect of light scattering (MFE_{LS}) in excited state. (c) UV-vis absorption spectrum of MYG, ligand (Y), as synthesized magnetic nanoparticles (MNP) and electrolytically exfoliated graphene.

15.3% respectively. The more complete orientation of MYG flakes can be generated in presence of a stronger magnetic field leading to larger scattering cross-section, according to equation (1). This is the key to enhance MFE_{LS} amplitude.

The MFE_{LS} of individual components of MYG are compared in **Figure 3-3c**. The MFE_{LS} of the ligands, the graphene flakes, and $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles were measured separately for this study. The ligand Y did not exhibit any notable MFE_{LS} while positive MFE_{LS} can be generated from electrolytically exfoliated graphene and $\gamma\text{-Fe}_2\text{O}_3$ magnetic nanoparticles (MNP). Pristine graphene suspension shows MFE_{LS} with lower amplitude (7%) than MFG suspension, while MNP shows the lowest amplitude around 3%. It has been shown that in graphene and its derivatives, defects such as vacancies, adatoms, and zigzag edges can introduce localized magnetic moments by the formation of unpaired spins leading to anisotropic magnetism¹²⁴⁻¹²⁷. We have previously reported that fluorinated graphene can be oriented by a magnetic field due to defect induced anisotropic magnetism, the MFE_{LS} results of electrolytically exfoliated graphene indicate that it may also incorporate such effects^{26, 51}. It should be noted that MFE_{LS} of superparamagnetic $\gamma\text{-Fe}_2\text{O}_3$ MNP shows much narrower line-shape, revealing that MNP possesses a larger magnetic susceptibility giving rise to a faster magnetic response²¹. By coupling MNP with graphene flakes through ligand Y, narrower MFE_{LS} line-shape and increase in MFE_{LS} amplitude can be observed in MYG suspension, indicating an enhancement of magnetic properties.

The excited state effect on magnetization in MYG particles has been studied with MFE_{LS} measurement by adding a 325nm excitation beam. The MFE_{LS} results of MYG suspension in ground state and excited state are given in **Figure 3-3d**. An increase in MFE_{LS} amplitude can be observed in MYG suspension with photoexcitation. Under 250mW/cm² photoexcitation, the MFE_{LS} amplitude increases from 12.2% to 14.8% in MYG suspension. In general, the 325nm pump beam can influence the MFE_{LS} amplitude through different channels including: interfering with the detection of scattered light, generating photoluminescence, changing solvent viscosity through heating, and enhancing magnetic properties through excited states. In our steady state pump-probe measurement, the pump beam and probe beam are completely separated in wavelength by the spectrometer. Thus, the pump beam (325 nm) does not affect the scattering detection of probe beam (532 nm) at any incident angle. Furthermore, the MYG particles do not have detectable photoluminescence under 325nm pump beam excitation, excluding the

possibilities of having photoluminescence in scattering detection. In addition, the viscosity of solvent may be changed due to the heat generated by the pump beam, leading to a change in MFE_{LS} signal. However, based on our experimental analysis, the temperature change upon photoexcitation is less than 1K, which is not sufficient to introduce an appreciable change in MFE_{LS} signal via variation of solvent viscosity²⁶. Therefore, the enhanced MFE_{LS} amplitude can be induced by the enhancement of magnetic properties through excited states in graphene or MNP. According to the MFE_{LS} result from graphene and MNP, 325nm photoexcitation does not cause a notable change on MFE_{LS} signal in MNP suspension as seen in **Figure 3-3e**. In **Figure 3-3f**, MFE_{LS} signal in graphene suspension increases from 7.2% to 8.2% upon 250mW/cm² photoexcitation. Therefore, the enhanced MFE_{LS} from both graphene and MYG under photoexcitation implies that MYG particles possess a stronger magnetization in excited state contributed by the excitation of the graphene part. It is known that delocalized π electrons can exhibit stronger electrical polarization in excited state based on molecular orbital theory. Due to the interaction between delocalized π electrons and localized spins in graphene flakes, it can be expected that a larger magnetization can be generated with enhanced electrical polarization in graphene under excited state. As a consequence, increased MFE_{LS} amplitude can be obtained from both graphene and MYG suspension upon photoexcitation due to the enhanced magnetization.

To better understand the excited state effect on magnetization of MYG particles, we analyzed the magnetic response by comparing MFE_{LS} line-shape in ground state and under different intensity photoexcitations. **Figure 3-4a** and **Figure 3-4b** are the MFE_{LS} results and normalized MFE_{LS} curves of MYG suspension under high intensity photoexcitation. Interestingly, increasing photoexcitation intensity leads to a narrower line-shape, in addition to the enhancement in MFE_{LS} amplitude in MYG suspension. However, no obvious line-shape narrowing phenomenon can be observed in the MFE_{LS} from graphene suspension under the influence of photoexcitation in **Figure 3-3f**. In general, a narrower line-shape implies that the orientation of suspended nanohybrid caused by magnetization occurs more easily due to magnetization under photoexcitation. Therefore, a line-shape narrowing phenomenon can provide an evidence that the magnetization becomes stronger under photoexcitation in the nanohybrid. Specifically, in the MYG nanohybrid, the graphene can interact with the γ -Fe₂O₃ nanoparticles through d- π electron coupling^{135, 136} based on (i) long-range Coulomb interactions and (ii) short-range spin-spin interactions between

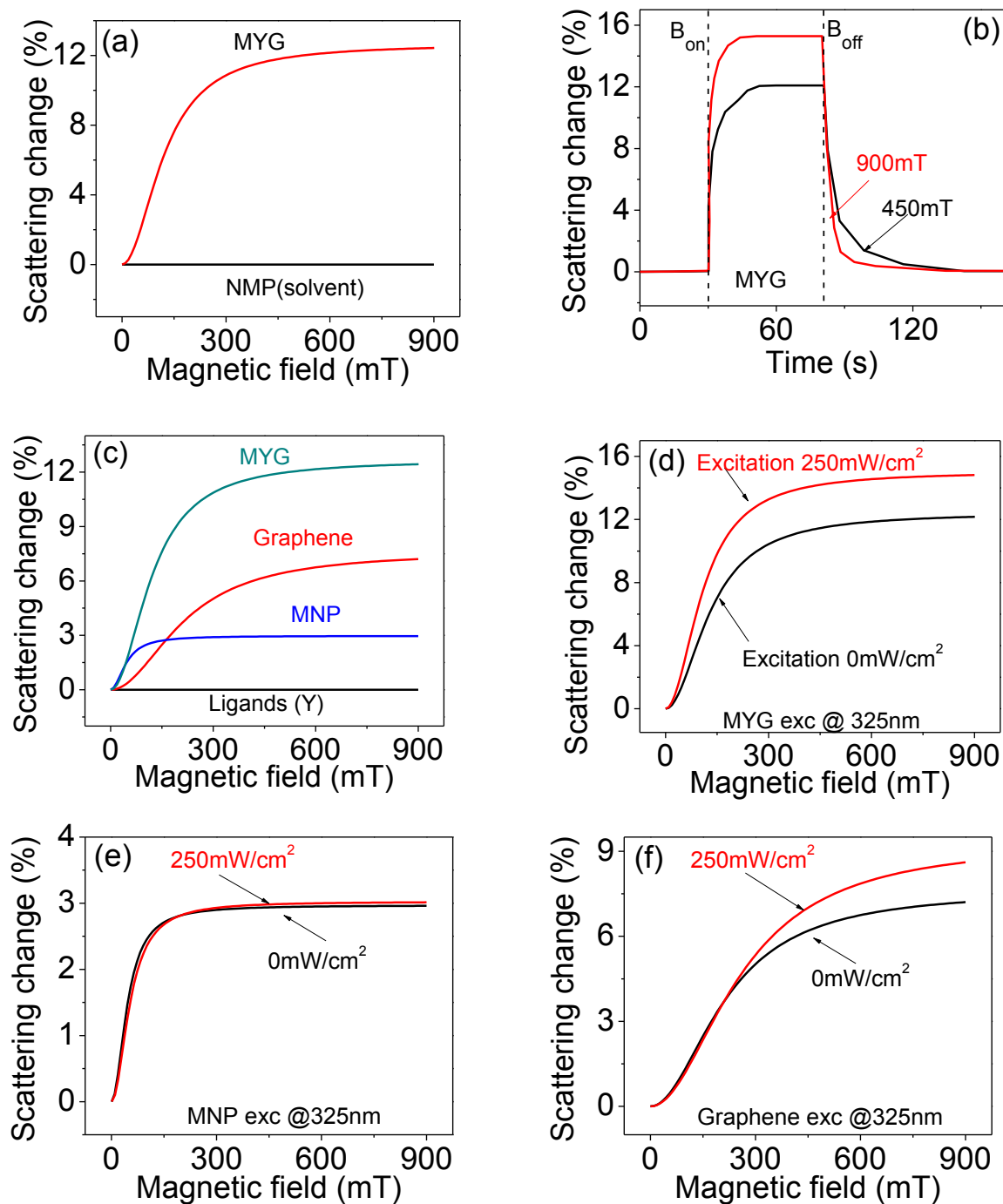


Figure 3- 3 (a) MFE_{LS} signals from magnetic nanoparticle functionalized graphene suspended in NMP with a concentration of 1mg/ml. (b) Time-dependent MFE_{LS} profile under different magnetic field (c) MFE_{LS} signals from the coupled sample (MFG) and separated components (MNP, graphene, organic molecules). (d) MFE_{LS} signals from MNP functionalized graphene in ground state and excited state. MFE_{LS} signals from (e) magnetic nanoparticles and (f) graphene.

magnetic d electrons and semiconducting π electrons^{136, 137}. When the MYG nanohybrid is placed in excited state upon photoexcitation, both Coulomb interaction and spin-spin interaction between d electron in $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles and delocalized π electron in graphene can be enhanced. Consequently, stronger magnetization can be generated in $\gamma\text{-Fe}_2\text{O}_3$ particles. Therefore, combining the superparamagnetic $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles with semiconducting graphene presents a convenient method to generate photoexcitation-controllable magnetization in the MYG nanohybrid.

Time-dependent MFE_{LS} results from MYG suspension at a fixed magnetic field in ground and excited state are shown in **Figure 3-4c** and **Figure 3-4d**. In time-dependent measurement, instead of gradually increasing the magnetic field, magnetic field is turned on and turned off immediately in order to analyze the magnetic response and relaxation of suspended particles in solvent. The MYG particle under photoexcitation exhibit a shorter response time orienting under the influence of the magnetic field and reaching a saturated scattering intensity of light as seen in **Figure 3-4d**. Also, the time for MYG particles to relax into random orientation is shorter in excited state. The magnetization of the MYG nanohybrid particles in solution by an applied magnetic field can lead to the gain of magnetic energy which can be defined as follows¹³⁸:

$$U = -\mu H \cos\theta - \frac{V\Delta\chi H^2}{2\mu_0} \cos^2\theta \quad (3-2)$$

Here μ is the magnetic moment, the orientation angle θ is the angle between magnetic moment and magnetic field. In the time-dependent measurement, the suspended MYG nanoparticles are located at the states with different magnetic energy, labeled as U_0 and U_B , representing their energy without and with external magnetic field, respectively. After magnetic field is removed, the relaxation of suspended MYG nanoparticles is essentially driven by the restoring torque τ , given by

$$\tau = \frac{\partial(\Delta U)}{\partial\theta} \quad (3-3)$$

where $\Delta U = (U_B - U_0)$. In excited state, the total energy U consists of two components: magnetic energy U_1 due to the magnetization of MYG nanoparticles in ground state, and the additional magnetic energy U_2 under photoexcitation. The restoring torque τ_{ex} in excited state then can be defined as

$$\tau_{ex} = \left(\frac{\partial U_1}{\partial \theta} \right) + \left(\frac{\partial U_2}{\partial \theta} \right) \quad (3-4)$$

When magnetic field is removed, the magnetic energy generated restoring torque can relax MYG particles back to random orientation. Clearly, a faster relaxation due to stronger restoring force suggests a larger magnetization of MYG particles in the excited state leading to a faster relaxation process as shown in **Figure 3-4d**.

To further understand the interaction between magnetic nanoparticles and the semiconducting graphene involved in photoexcitation-controllable magnetization, the effect of mixing MNPs into MYG and pristine graphene suspension liquids were examined. This is crucial in establishing the importance of assembling the van der Waals heterostructure of graphene and ligand functionalized γ -Fe₂O₃ MNPs. Both MYG and graphene suspensions were loaded with a higher concentration of as-synthesized MNPs and their MFE_{LS} were measured. The results from the MYG dispersions containing an added 0.1mg/ml of MNPs are given in **Figure 3-5a**. The result shows that MFE_{LS} signals can be further increased by the addition of MNPs. Furthermore, the line-shape of MFE_{LS} becomes narrower by adding MNP particles into MYG suspension as shown in the normalized MFE_{LS} in **Figure 3-5b**. The addition of MNPs to MYG can lead to complex interactions between the magnetization of free suspended superparamagnetic MNPs and the MNPs immobilized on graphene. The superior magnetic susceptibility of the MNPs lead to larger magnetization, this would mean that increasing the density of MNPs non-covalently assembled on graphene would lead to a faster response in the MYG particle. The density of nanoparticles on the surface of the graphene is controlled by conditions of self-assembly of the nanohybrid and should be optimized during the synthesis of MYG. Interestingly when 0.1 mg/ml MNP is added into pristine graphene dispersion, the MFE_{LS} amplitude only increases slightly, while the line-shape becomes broader as shown in **Figure 3-5c** and **Figure 3-5d**. This means that the magnetization of the sample became gradual on addition of MNPs. In the absence of the ligand mediating the attachment of MNPs to the surface of graphene, the possible interaction between the MNPs and graphene would be through residual carboxylic or hydroxyl groups on the surface of graphene¹³⁹. Such an interaction is non-specific and random leading to sparse interaction between MNPs and graphene sheets and hence slower response to magnetism. In this scenario, it can be concluded that the MFE_{LS} amplitude increase shown in the case of MYG hybrid (**Figure 3-5a**) indicates additional interaction between the suspended MNPs and those assembled on graphene. Moreover, the MFE_{LS}

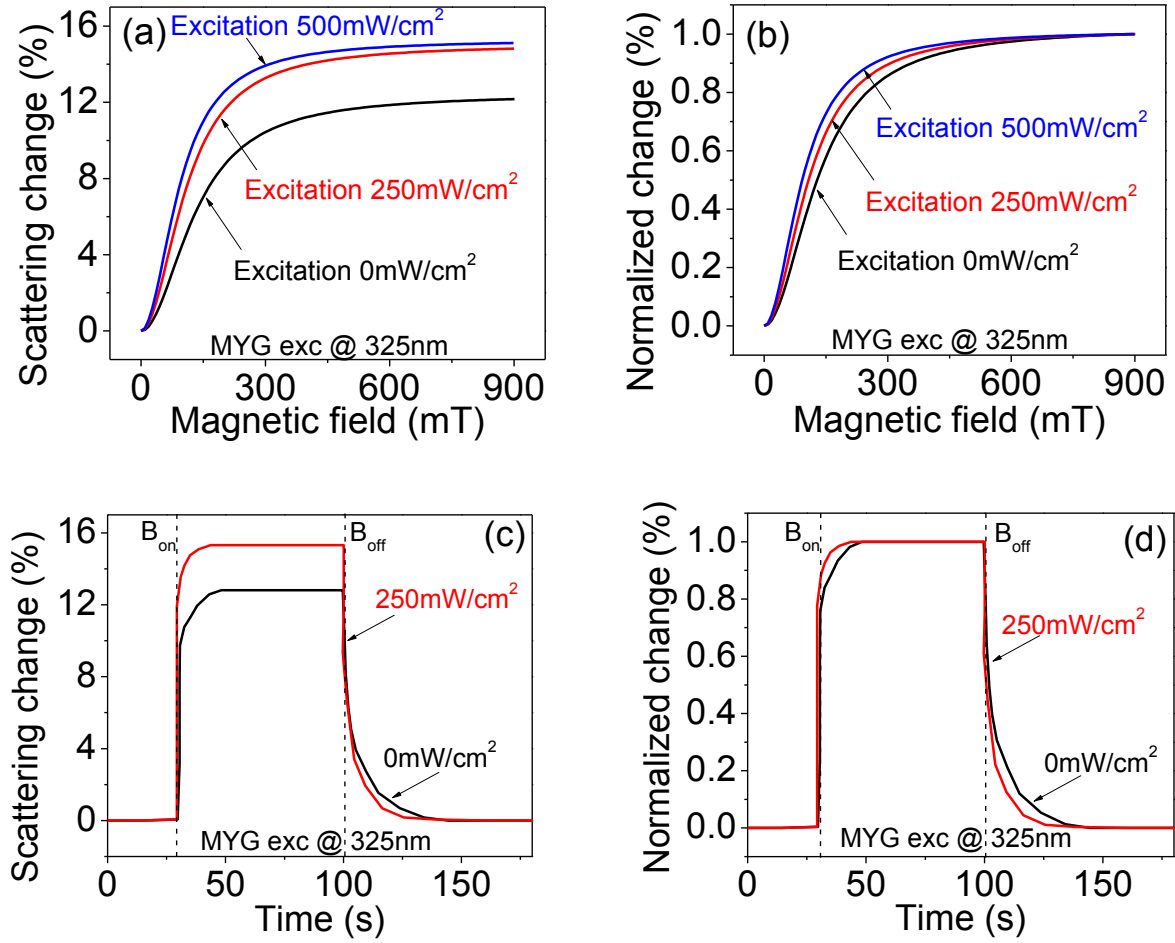


Figure 3- 4 (a) MFE_{LS} signals from MYG in ground and excited states, (b) normalized MFE_{LS} curve of MYG in ground state and excited state. Time-dependent profile of MFE_{LS} signals from MYG under (c) ground state and (d) excited state.

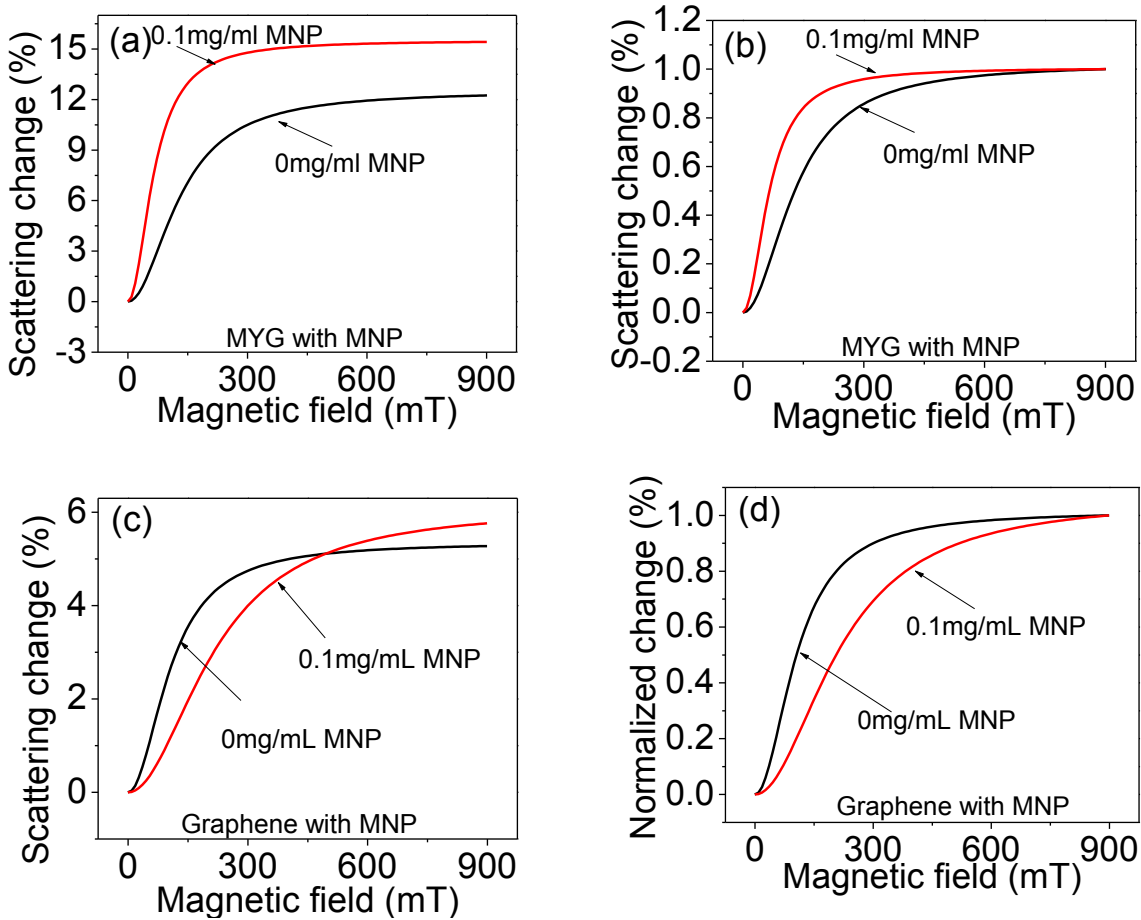


Figure 3- 5 (a) MFE_{LS} signals from MFG with MNP added. (b) normalized MFE_{LS} curves of MFG with MNP added. (c) MFE_{LS} signals from graphene with MNP added. (d) normalized MFE_{LS} curves of graphene with MNP added.

results presented in this study imply that the ligand (Y) mediated non-covalent assembly of MNPs on to graphene in the nanohybrid MYG leads to enhanced anisotropic magnetism.

3.5 Summary

In summary, we experimentally study the magnetic properties of $\gamma\text{-Fe}_2\text{O}_3$ /graphene hybrid materials by using magnetic field effect of light scattering. Our study shows that scattered light intensity from the $\gamma\text{-Fe}_2\text{O}_3$ /graphene nanohybrid suspension can be enhanced upon applying magnetic field due to the orientation of MYG particles under external magnetic field. Specifically, we find that by chemically bonding graphene with MNP, the coupled sample can show a much faster magnetic response as compared to pristine graphene. We observe that the amplitude of MFE of scattering from MYG suspension can be enhanced upon applying excitation beam, which indicates that photoexcitation can induce enhanced magnetization due to the interaction between delocalized π electrons and localized spins in graphene. Furthermore, loaded with a higher concentration of as-synthesized MNPs, MYG, and graphene, show enhanced and deteriorated magnetic response, respectively. This result provides evidence that mediated non-covalent assembly of MNPs on to graphene through ligands in the nanohybrid MYG can lead to enhanced anisotropic magnetism. Clearly, by using MFE of light scattering with the pump-probe method, our studies provide a deeper understanding on the coupling between magnetic and semiconducting properties in nanohybrid with 0D-2D heterostructures.

Chapter 4 Optically Tunable Spin-orbital Coupling Effects in Metal Halide Perovskites Solar Cell based on Polarized Photoexcitation

4.1 Abstract

Hybrid metal halide perovskites have emerged as promising materials for photovoltaic and light emitting applications. These materials also show great potential for the spintronics due to their strong spin orbit coupling, and Rashba effect. Under the influence of strong spin-orbital coupling, photo-generated excited states in metal halide perovskites possess both orbit momentum and spin momentum with total angular momentum $J=L+S$. Manipulating spin and orbit parameters in perovskites offers unique opportunities to generate different multifunctional properties. However, generating J polarized excited states and detecting the interaction between polarized excited states in perovskite remain un-addressed issues. In this chapter, polarized photoexcitations are used to generate electron-hole pairs with different orbit momentums. Our results indicate the SOC of hybrid perovskite can be optically tuned through orbit-orbit interaction, and consequently generating different bright-to-dark state conversion through SOC. Based on the optically tunable SOC, the charge dissociation and recombination process in hybrid perovskite can be manipulated by switching photoexcitation polarization. The important precondition for optically manipulating SOC in electron-hole pairs is discussed by comparing the spin lifetime, recombination lifetime and dissociation lifetime of MAPbI₃.

4.2 Introduction

Metal halide perovskites have attracted extensive attention in the past decade as active layers in photovoltaic devices due to their excellent optoelectronic properties, such as: high carrier mobility¹⁴⁰⁻¹⁴², large light absorption coefficient in visible range¹⁴³⁻¹⁴⁵, and long charge carrier diffusion length¹⁴⁶⁻¹⁴⁹. Specifically, due to the strong SOC of metal hybrid perovskites, the orbit motion and spin of carriers are strongly coupled, the total angular momentum $J = L + S$ must be considered. Thus, in hybrid perovskites, the excited states are referred to J states, different from spin singlets and spin triplets in organic materials where orbit momentum is absent. It has been reported that, under the influence of strong SOC and electron-hole exchange interaction, the fine structure of band edge excitons in MHPs can have recombination allowed triplet states, and recombination disallowed singlet state, namely, bright state ($J = 1$) and dark state ($J = 0$). The magnetic field effect studies on MHPs have shown that bright and dark states have different dissociation and recombination processes. Tuning bright state and dark state population ratio by applying magnetic field can lead to field-dependent photocurrent, photoluminescence,

electroluminescence and electric polarization^{76, 77, 150-152}. In principle, electron hole pairs generated by polarized photoexcitation possess orbital field through orbital momentum transfer. The SOC can be possibly tuned when the electron hole pairs interact with each other with regard to their orbit fields.

In this chapter, the magneto-photocurrent of perovskite solar cells is studied by using polarized photoexcitation. Different line-shape of MFE is observed between linear and circular polarized photoexcitation. This indicates that the spin mixing due to SOC can be essentially changed by switching photoexcitation polarization. Polarization-dependent photocurrent confirms that SOC can be essentially tuned by switching photoexcitation polarization through orbit-orbit interaction, which leads to optically controllable photovoltaic actions. Transient absorption and PL lifetime are measured to analyze the necessary condition for generation of optically tunable charge recombination and dissociation process in perovskites.

4.3 Materials and Methods

4.3.1 Device fabrication

All solar cells studied in this work were fabricated with a planar structure of ITO/NiOx/perovskite/PCBM/PEI/Ag (**Figure 4-1a** and **Figure 4-1b**). The PEDOT: PSS layer was spin-cast on top of pre-cleaned indium tin oxide (ITO) substrates at 4000 rpm for 90 seconds and then annealed at 300 °C in ambient conditions for 60 min. The MA-based perovskites were prepared from the precursor solutions of MAPbI₃ (1.3 M) by dissolving methylammonium iodide (MAI, from 1-Material), and lead (II) iodide (PbI₂, from Alfa Aesar). The mixed solvent of γ -butyrolactone (GBL) and dimethyl sulfoxide (DMSO) (7:3 v/v, from Sigma-Aldrich) was used for the precursor solutions, which were stirred at 65 °C for 12 h and then cooled to room temperature before using. The perovskite thin films were spin-cast on top of NiOx with a two-step spin-coating process (1000 rpm for 10 s and 4000 rpm for 40 s). The substrates were subjected to a fast antisolvent extraction process with toluene (400 μ L) at the 20th second of the second step, followed by thermal annealing at 100 °C for 10 min. The PC₆₁BM layer was coated on top of the perovskite layer at 2000 rpm for 60 s from a 20 mg/mL solution of chlorobenzene (from Sigma-Aldrich); the substrates were then kept in a glass Petri dish for 45 min. Afterward, a solution of PEI (M_w ~2000, 50 wt % in water) in isopropyl alcohol (0.5 mg/mL) was spin-cast on top of the PCBM at 5000

rpm for 60 s. Finally, a 100 nm silver layer was thermally deposited as the cathode with an effective area of 0.075 cm² under a vacuum of 7×10^{-7} Torr.

4.3.2 Characterization and magnetic field effect measurements

The PL measurements were performed by SPEX Fluorolog III spectrometer. The current density-voltage (J-V) characteristics of perovskite solar cells were measured in a nitrogen-filled glove box by using Keithley 2602 source meter under simulated sunlight (AM 1.5G, Thermal Oriel 96000 300 W, Newport). Before experimental measurements, the devices were illuminated with simulated sunlight for 30 minutes to remove light soaking for developing stable J_{SC} and V_{OC}. The magneto-photocurrent measurements were performed by recording the photocurrent as a function of magnetic field (B, ~900 mT), which was applied parallel to the device plane. The magneto-photoluminescence measurements were performed by recording the photoluminescence as a function of magnetic field with the same setup through Fluorolog III spectrometer (**Figure 4-1c**). The magneto-photocurrent and magneto-photoluminescence signal (%) is defined by $MFE = \frac{I_B - I_0}{I_0} \times 100\%$, where I_B and I_0 represent the photocurrents (or photoluminescence) with and without magnetic field, respectively. The curve shape of MFE can be fitted by a Lorentzian function: $MFE = A \frac{B^2}{B^2 + B_0^2}$ where A is the coefficient, B is the applied magnetic field, and B₀ corresponds to the internal magnetic interaction. The control-experiment was done by using organic solar cells with the planar structure of ITO/PFN/PCBM: PTB7/MoO₃/Ag.

4.3.3 Polarization-dependent photocurrent and photoluminescence measurements

The spin effect on light emission and charge dissociation is studied by detecting photoluminescence and photocurrent when photoexcitation is switched between linear and circular polarization. The measurement setup is shown in **Figure 4-2**. Linear polarized light is first produced when laser propagating through a linear polarizer. Then the polarization of the laser can be tuned by rotating the quarter wave-plate at 0° and 45° for linear and circular polarization. The light is then applied to the sample surface with normal incidence (normal to the sample plane). Based on Fresnel equations, the reflectance of linear polarized light (with and polarization direction) and circularly polarized light should be identical at normal incident. The absorption of

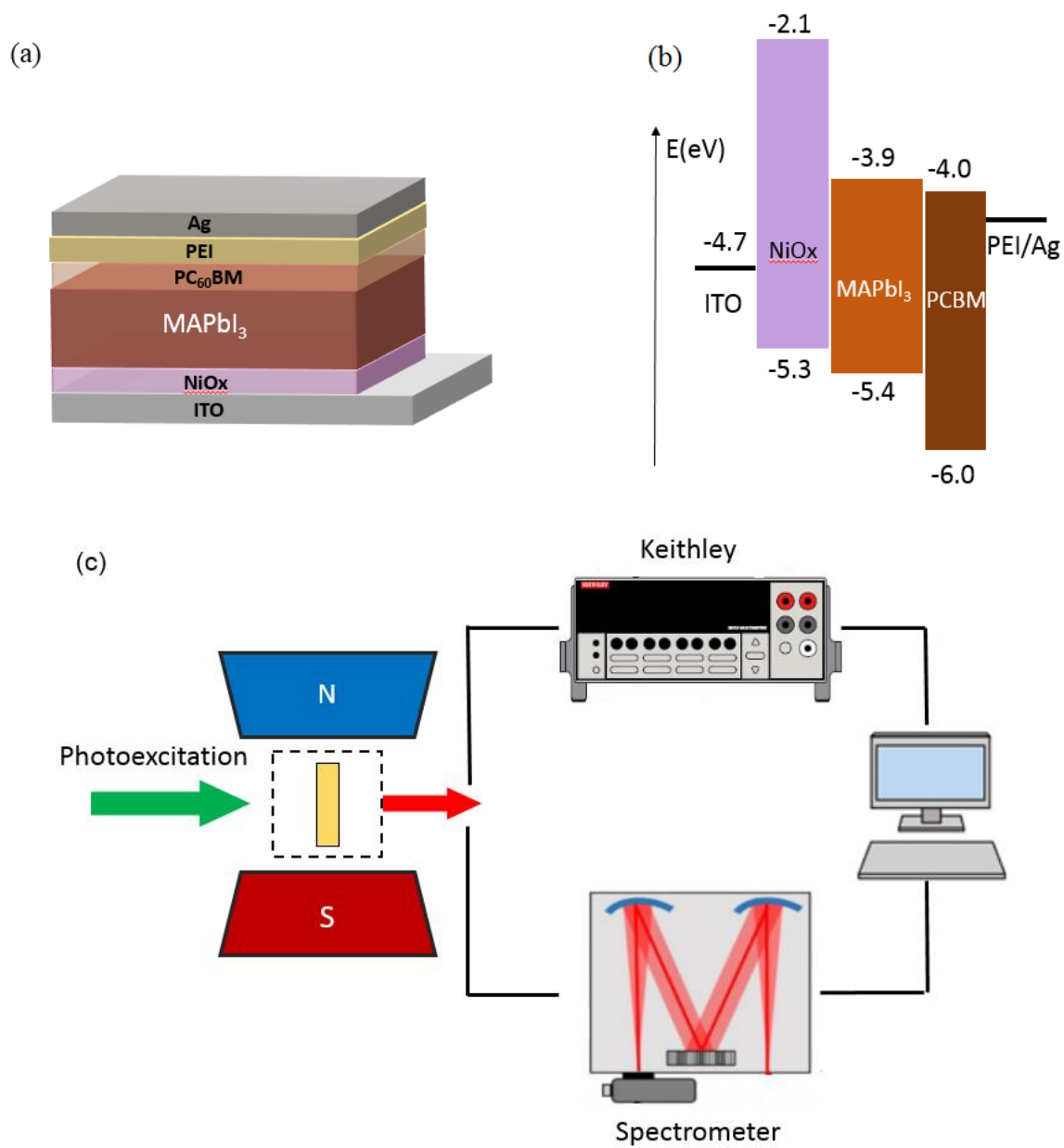


Figure 4- 1 (a) schematic diagram of perovskite solar cell. (b) Energy level diagram of perovskite solar cell. (c) Schematic of magnetic field effect measurements.

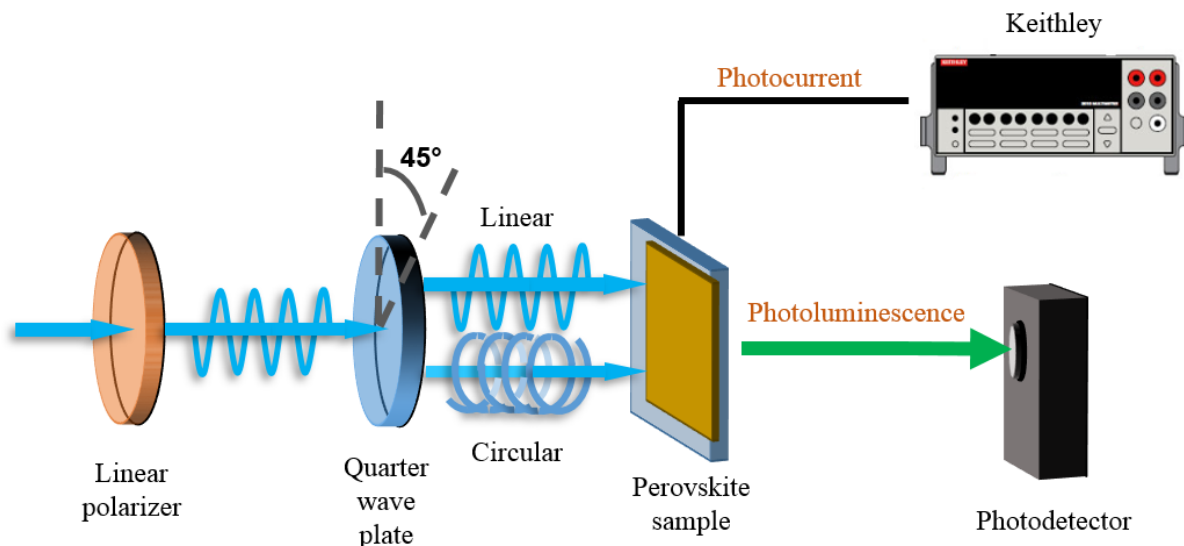


Figure 4- 2 Measurement setup for polarization-dependent J_{sc} and PL in metal halide perovskites by switching photoexcitation polarization.

linear and circular light for perovskite sample should also be identical due to the same incident light intensity and the same reflectance. To minimize the experimental error caused by the optics and the optics alignment, the measurement setup is calibrated with a silicon photodetector (Thorlab APD120A, 200-1000nm). By switching photoexcitation polarization, the change in J_{sc} should be lower than 0.05%. During measurement, the photoluminescence is collected by optical fiber and direct to the spectrometer, and the photocurrent is measured by Keithley 2400.

4.4 Results and Discussion

The planar metal halide perovskite (MHP) solar cells with device structure of ITO/NiO_x/MAPbI₃/PC₆₀BM/PEI/Ag are fabricated via anti-solvent process (**Figure 4-3a**). The current-voltage (J-V) characteristics of the devices under AM 1.5G irradiation are shown in **Figure 4-3b**. The device exhibits power conversion efficiency (PCE) of 17.7%, with a short-circuit current (J_{sc}) of 22.99 mA/cm², an open-circuit voltage (V_{oc}) of 1.07V, and a fill factor (FF) of 72%. The absorption and PL spectrum are shown in **Figure 4-3c**. The absorption onset is at 785nm, which is consistent with the bandgap of MAPbI₃ around 1.55eV. The typical MAPbI₃ emission peak at 780nm can be observed in the photoluminescence spectrum.

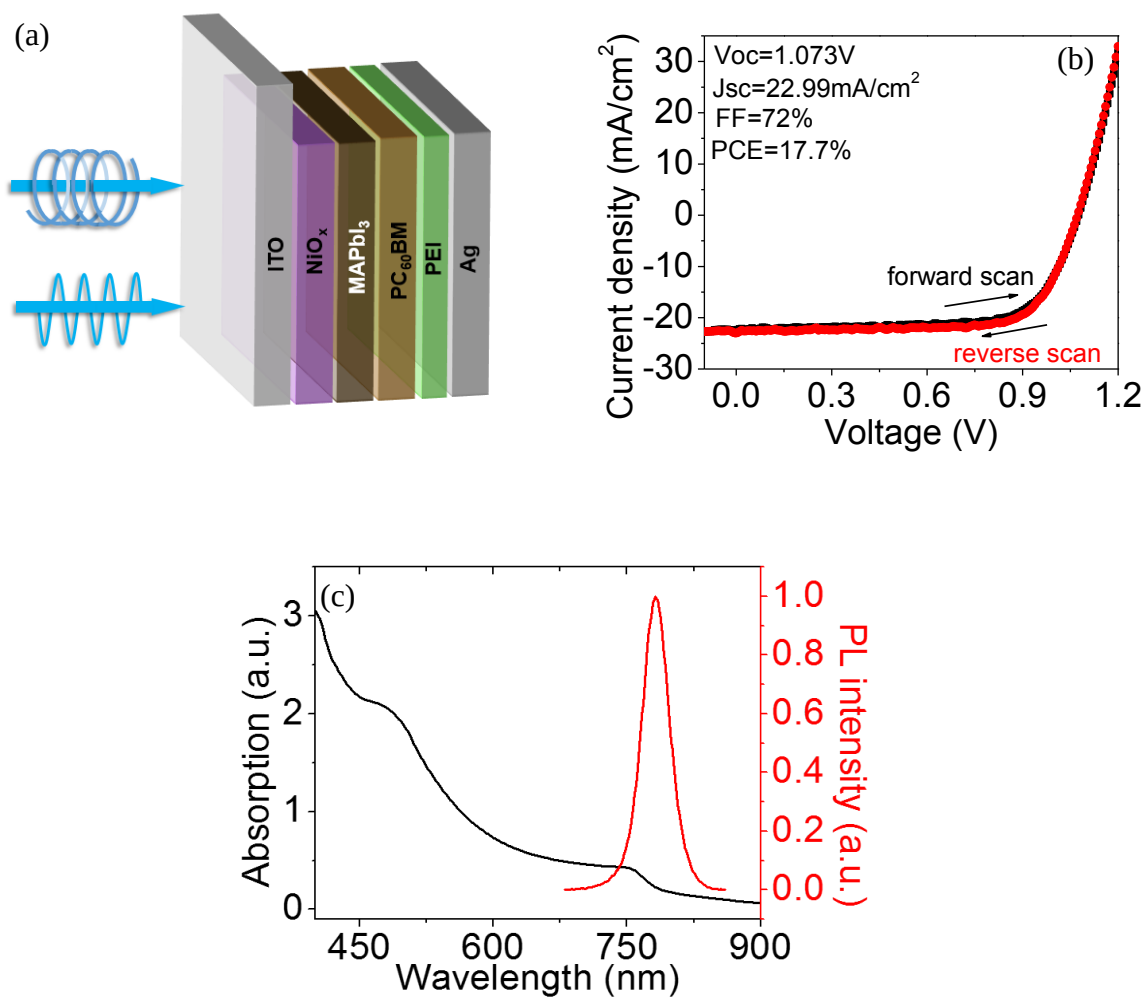


Figure 4- 3 (a) Device structure of MAPbI₃ based solar cell. (b) Current-voltage characteristics of MAPbI₃ based solar cell. (c) Absorption and photoluminescence spectrum of MAPbI₃ thin film.

Figure 4-4 shows the magneto-photocurrent under linearly and circularly polarized 488nm continuous-wave laser excitation in MHP solar cells. The 488nm laser beam is switched between linear and circular polarization through a quarter wave-plate with identical intensity. We can see that the photocurrent increases with increasing the magnetic field strength, leading to a positive magneto-photocurrent. Here, the magneto-photocurrent amplitude is defined as: $MFE = (I_B - I_0)/I_0$, where I_B and I_0 are the photocurrents with and without external magnetic field. It should be noted that $J = 1$ electron hole pairs ($|\psi_{1,+1}\rangle$, $|\psi_{1,0}\rangle$, $|\psi_{1,-1}\rangle$) are generated under photoexcitation. These electron hole pairs can be partially converted into $J = 0$ ($|\psi_{0,0}\rangle$) electron hole pairs through spin mixing due to the strong spin-orbital coupling (SOC) arise from heavy elements, leading to coexisting of bright states ($J=1$) and dark states ($J=0$). Meanwhile, exchange interaction in electron hole pairs can serve as spin conserving disallowing interconversion between bright and dark states. The competition between exchange interaction and SOC can reach equilibrium in the population ratio of bright and dark states. Since bright state and dark state have different dissociation rates. An external magnetic field can change the bright state/dark state population ratio by suppressing spin mixing, and consequently modify the photocurrent, generating magneto-photocurrent. Furthermore, the line-shape of magnetic field effect can represent how fast the external magnetic field can change the bright state/dark state ratio in generating MFE response.

It is interesting to note that, the line-shape of magneto-photocurrent becomes slightly broader when photoexcitation is switched from linear and circular polarization with low intensity (**Figure 4-4a**). By increasing photoexcitation intensity (120mW/cm^2) (**Figure 4-4b**), the difference in line-shape of magneto-photocurrent becomes larger when between linear and circular photoexcitation. Basically, the line-shape of MFE can represent how fast the singlet/triplet ratio changes under external magnetic field. We should note that spin mixing induced by SOC and spin conserving due to exchange interaction allows and disallows the interconversion of bright and dark states, respectively. The competition between spin mixing and spin conserving leads to an equilibrium on the populations between spin-singlet and spin-triplet electron hole pairs. When the external magnetic field is comparable to the internal magnetic interaction, it can disturb the equilibrium and consequently change the bright state/dark state ratio. In our measurements, by switching the photoexcitation between linear and circular polarization, the exchange interaction determined by the Coulomb interaction for electron hole pairs are identical due to the same excitation intensity. Therefore, the line-shape of MFE can be essentially determined by SOC. Here,

the magneto-photocurrent curve can be fitted by a Lorentzian function: $MFE = A \frac{B^2}{B^2 + B_0^2}$, where A is the coefficient, B is the applied magnetic field, and B_0 corresponds to the internal magnetic interaction from SOC. It can be numerically analyzed that the B_0 under 48mW/cm² linearly polarized photoexcitation (B_{0L}) is 207.6mT, while the B_0 under 48mW/cm² circularly polarized photoexcitation (B_{0C}) is 218.1mT. At 120mW/cm² photoexcitation intensity, B_{0L} is 177.4mT, and B_{0C} is 261.5mT. It can be observed external magnetic field are competing with much different internal magnetic interaction to generate MFE between linear and circular photoexcitations, and lead to a significant difference in MFE line-shape. This suggests that SOC for circular photoexcitation generated electron hole pairs is larger than that under linear photoexcitation. To verify the influence of SOC on MFE line-shape in MHP solar cells, the MFE of MAPb_{0.5}Sn_{0.5}I₃ based MHP has been measured and shown in **Figure 4-4d**. The Pb is partially substituted by Sn with lighter atomic weight. The MAPb_{0.5}Sn_{0.5}I₃ solar cells show a narrower line-shape of magneto-photocurrent as compared to Pb based MHP solar cells with the same excitation intensity. Clearly, this observation suggests that the line-shape of magneto-photocurrent in MHP devices are mainly controlled by SOC. According to this scenario, electron-hole pairs generated by linearly and circularly polarized photoexcitation can exhibit different SOC leading to the change in line-shape of magneto-photocurrent.

It has been studied that under the influence of strong SOC, the band structure of MHPs is modulated to form a non-degenerate conduction band with $J=3/2$ and $J=1/2$, and valance band with $S=1/2$, where J is the total angular momentum quantum number. Specifically, in metal (Pb) halide(I, Br) perovskites, the conduction band (CB) is constituted of the Pb-p orbitals, while the valence band (VB) is originated from the hybridized anti-bonding state between Pb-s and halide-p orbitals, which retains the s symmetry. Thus, excited electrons can have strong orbit momentums due to SOC. Under circularly polarized photoexcitation, the excited electrons are moving on the orbitals with the same direction. As a result, the excited electrons have same-directional magnetic dipole momentums. On the other hand, when a linearly polarized photoexcitation is applied, which equivalent to the combination of left-hand (σ^+) and right-hand (σ^-) polarized photoexcitations, the excited electrons are moving on their orbitals with opposite direction, leading to opposite-directional magnetic dipole momentums. When the excited electrons moving on adjacent orbitals encounter a mutual interaction, same-directional and opposite-directional magnetic dipole

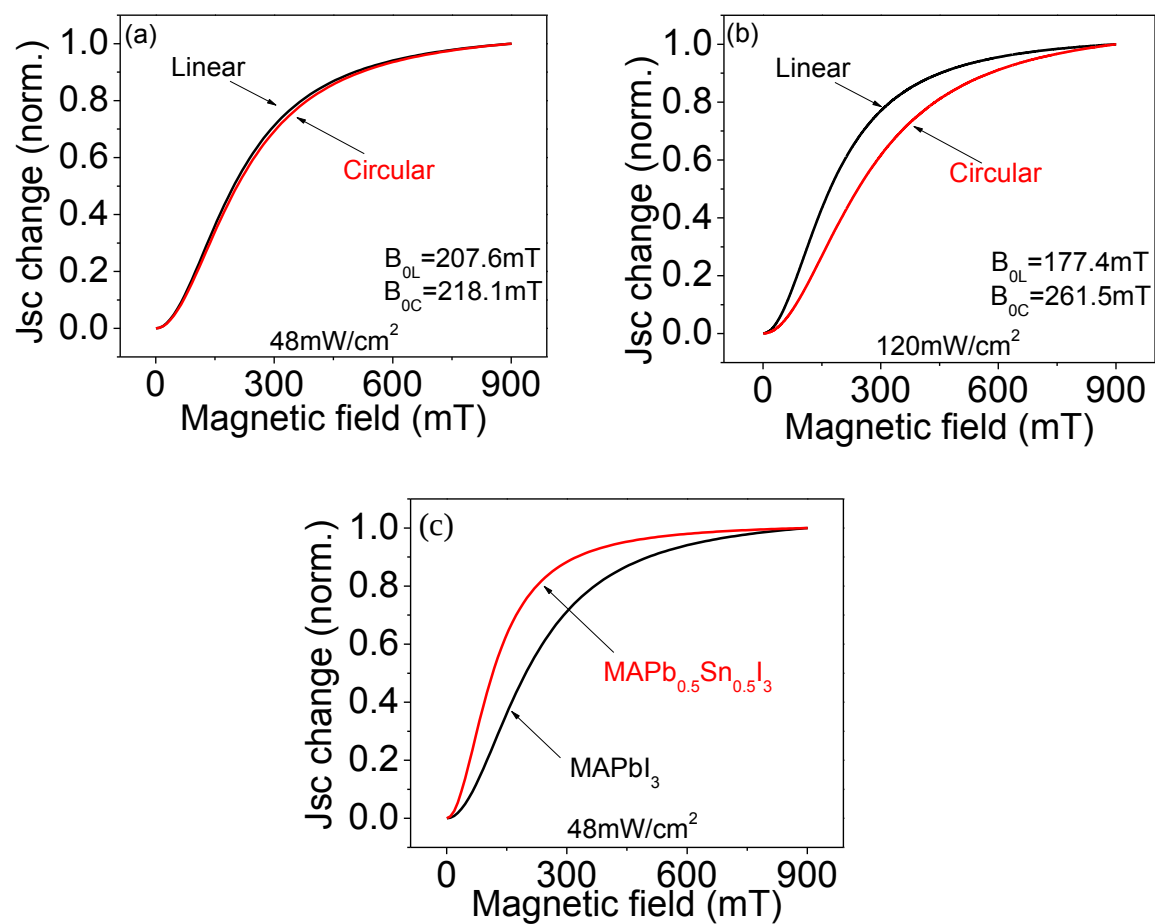


Figure 4- 4 Normalized MFE_{PC} curves of MAPbI₃ based solar cells under linear and circular excitation (a) 48mW/cm², (b) 120mW/cm², (c) 240mW/cm², (d) Normalized MFE_{PC} curves of MAPbI₃ and MAPb_{0.5}Sn_{0.5}I₃ based solar cells under 48mW/cm² photoexcitation.

momentums combine into stronger and weaker total momentums, respectively. This leads to higher and lower spin-orbit coupling under circular and linear photoexcitations. As a consequence, a change in SOC(Δ SOC) can be induced by switching the photoexcitation between linear and circular polarization. At low excitation intensity, the light polarization induced SOC difference is relatively small due to relative weak orbit-orbit interaction with less excited orbits. By increasing the excitation intensity, the SOC difference becomes more significant due to the enhanced orbit-orbit interaction between photo-generated electron-hole pairs, consequently a larger difference in line-shape of MFE can be observed.

To further confirm the photoexcitation polarization effect on SOC, we perform the time-dependent J_{sc} measurement on MHP solar cell by switching photoexcitation between linear and circular polarizations. It can be seen in **Figure 4-5a**, the J_{sc} increases from 1.586mA/cm² to 1.602mA/cm² by 0.98% upon switching photoexcitation from linear to circular polarization with 48mW/cm² intensity. Clearly, the photovoltaic action can be modulated by switching the photoexcitation polarizations with the same intensity, which indicates that the existence of an interaction between polarized light generated electron-hole pairs. In particular, more recombination forbidden dark electron hole pairs are generated under circularly polarized photoexcitation through enhanced spin mixing process due to the stronger SOC, while more bright state electron hole pairs are maintained under linear polarized photoexcitation due to the weaker SOC (**Figure 4-5b**). As a result, lower and higher J_{sc} values can be obtained when switching photoexcitation between circular and linear polarizations. The ΔJ_{sc} of 1.4% can be obtained under 120mW/cm² photoexcitation, as shown in **Figure 4-5c**. It is worth noting that the J_{sc} change (ΔJ_{sc}) shows a similar dependence on photoexcitation intensity comparing with the line-shape difference of magneto-photocurrent upon switching photoexcitation polarizations (**Figure 4-5d**). The photoexcitation intensity dependent ΔJ_{sc} upon switching photoexcitation polarization provides further evidence that the orbit-orbit interaction is enhanced by increasing density of excited orbits.

Now we verify that the photo-generated electron-hole pairs in MHP exhibit different SOC regarding to the incident light polarization through angular momentum transfer. The magneto-photocurrents under different polarized photoexcitation have been measured with photoexcitation intensity of 120mW/cm² based on organic solar cells with device structure of ITO/PFN/PCBM:

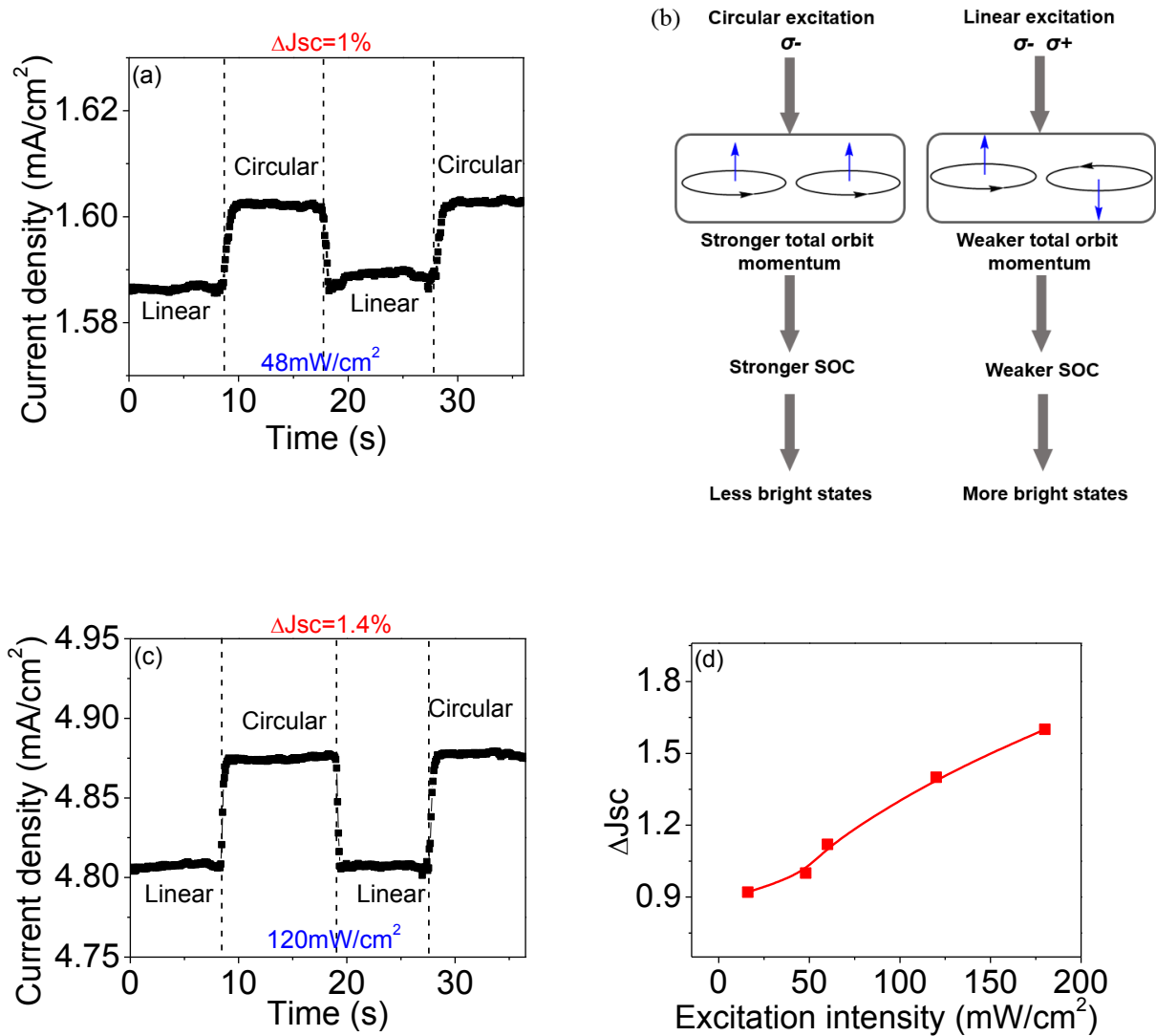


Figure 4- 5 (a) Short-circuit current density of MAPbI₃ solar cells recorded by switching photoexcitation polarization at 48mW/cm². (b) Schematic diagram of polarization dependent photocurrent. (c) Short-circuit current density of MAPbI₃ solar cells recorded by switching photoexcitation polarization at 120mW/cm² (d) Excitation intensity dependence of ΔJsc between linearly polarized excitation and circularly polarized excitation in MAPbI₃ solar cells.

PTB7/MoO₃/Ag. **Figure 4-6a** shows that the line-shape of magneto-photocurrent under linearly and circularly polarized photoexcitation are identical in organic solar cells. It is known that organic semiconductors with negligible SOC can be excited by polarized photoexcitation to generate spin antiparallel electron hole pairs due to spin selection rule. Angular momentum transferring process is not involved during photoexcitation, since the orbit momentum of electron or hole can only be zero. Obviously, photo-generated electron hole pairs in organic solar cells have no orbital momentum contributor. Consequently, orbit-orbit interaction cannot occur between electron-hole pairs. In addition, the time-dependent J_{sc} upon switching photoexcitation polarization has been studied in organic solar cells. It can be seen in **Figure 4-6b**, the change of J_{sc} between linear and circular photoexcitation is around 0.02%, which is within experiment error. The ΔJ_{sc} does not show an appreciable dependence on photoexcitation intensity (**Figure 4-6c**). This can also be understood that the electron hole pairs generated by linearly and circularly polarized photoexcitation in organic solar cells are subjected to the same spin mixing process from the intrinsic internal magnetic interactions, leading to almost identical singlet/triplet ratio, and consequently the photocurrents show a negligible difference. These results indicate that the light polarization induced change in SOC lies in the requirement of semiconducting materials with strong SOC modulated band structure where the angular momentum transfer can occur during photoexcitation process.

Based on the study of photoexcitation polarization modulated charge dissociation process in MHP solar cell above, now we analyze the photoexcitation polarization effect on the recombination process. **Figure 4-7a** shows photoluminescence change by switching photoexcitation polarization (ΔPL). In contrast to the results of ΔJ_{sc} measurement, the ΔPL measurements upon switching photoexcitation between linear and circular polarization do not show any appreciable change in PL intensity. We should note that photo-generated electron hole pairs can go through dissociation process to generate photocurrent or radiative recombination process. Research has shown that the spin lifetime for free electron and hole in perovskite are 5ps and 1ps at room temperature⁷⁵. When the electron hole pairs dissociate within the spin lifetime, ΔJ_{sc} can be observed upon switching photoexcitation polarization. Similarly, when the spin lifetime is comparable to the recombination lifetime, ΔPL can be observed upon switching photoexcitation polarization under steady state measurement. The dissociation time of photo-generated electron hole pairs in MAPbI₃ thin film

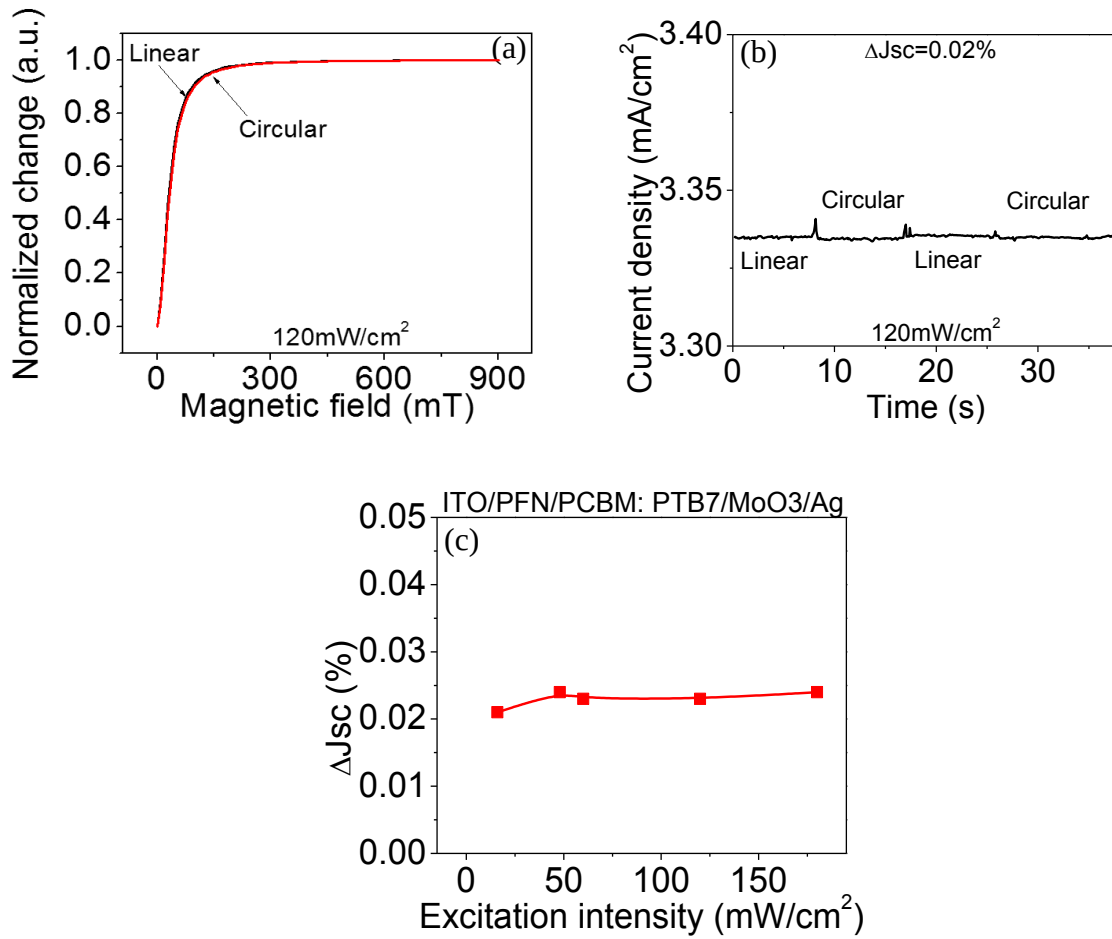


Figure 4- 6 (a) MFE_{PC} curves of organic solar cells with device structure of ITO/PFN/PCBM: PTB7/MoO₃/Ag under different polarized photoexcitations. (b) Short-circuit current density of organic solar cells recorded by switching photoexcitation between linearly polarized light and circularly polarized light excitation at 120 mW/cm². (c) Short-circuit current density change of organic solar cells by switching light polarization as a function of photoexcitation intensity.

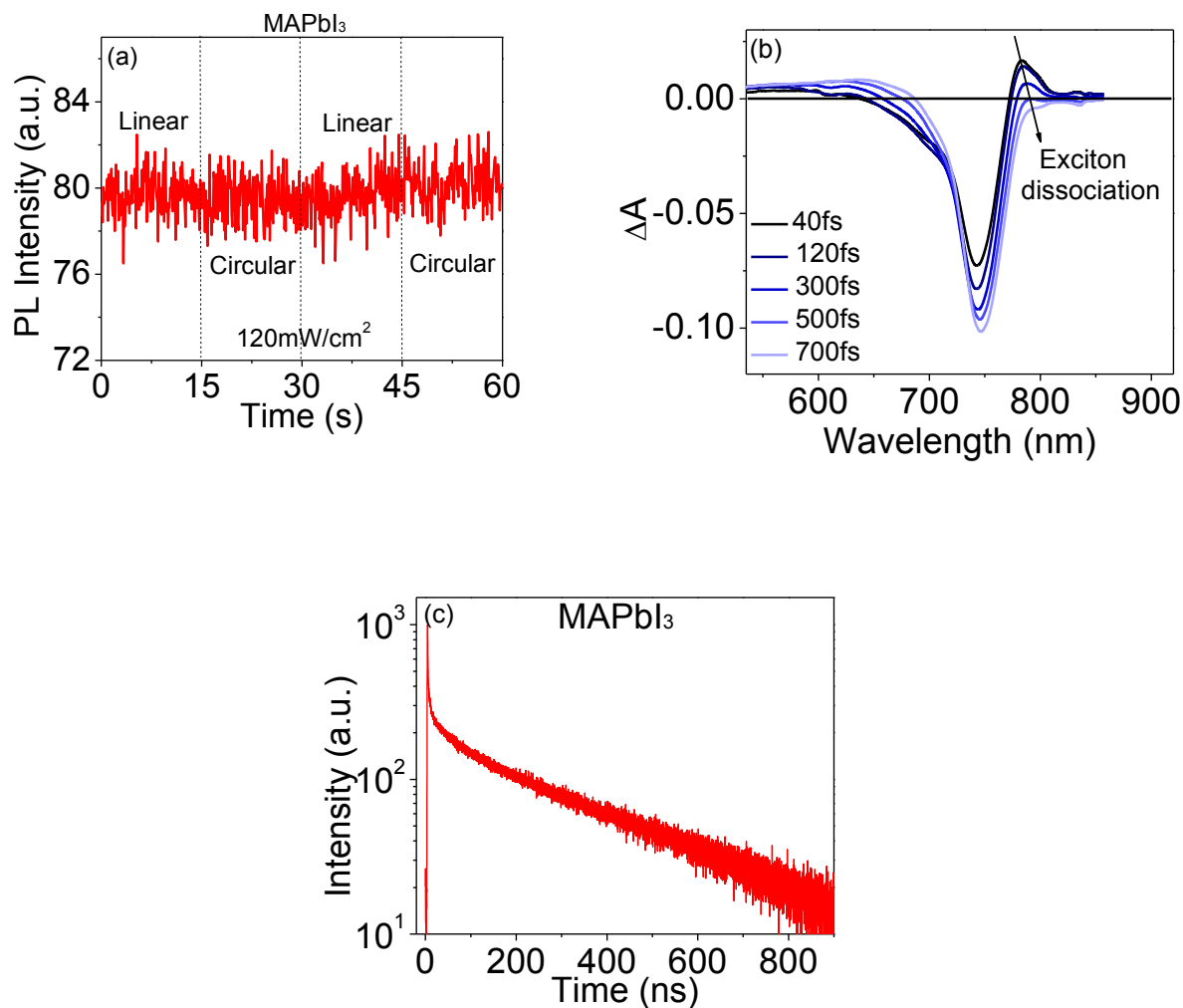


Figure 4- 7 (a) Photoluminescence intensity of MAPbI₃ thin film on a quartz substrate recorded by switching photoexcitation between linearly polarized excitation and circularly polarized excitation at 120mW/cm². (b) Transient absorption spectra of MAPbI₃ thin film on a quartz substrate at different delay times up to 1 ps. (c) PL lifetime of MAPbI₃ thin film on a quartz substrate.

has been studied by transient absorption spectra and shown in **Figure 4-7b**. The typical dissociation time is around 500 fs. The PL lifetime shown in **Figure 4-8b** indicated that the electron hole pairs in MAPbI₃ thin film can have PL decay time around 900 ns. Clearly, the fast dissociation process in MHP enables that J_{sc} change due to the polarized excitation induced population difference between bright and dark states. Meanwhile, the dissociated electrons and holes can be recaptured to form electron hole pairs, and then generated photoluminescence through bimolecular recombination. Since this process is much longer than spin relaxation process, negligible PL change under upon switching photoexcitation polarization can be observed. A recent study reported much spin relaxation time around 1ns for electron and hole in excitonic states of polycrystalline MHP. This suggests a potential approach to obtain photoexcitation dependent photoluminescence in low dimensional perovskites, in which photogenerated states are mainly geminate excitons due to large binding energy.

4.4 Summary

In this chapter, we explore the optical manipulation of spin and orbit parameters in metal halide perovskites by using polarized photoexcitations. The MFE curve-shape difference between linear and circular photoexcitations indicates an optically induced SOC change through orbit-orbit interaction. Based on orbit-orbit interaction, linear and circular photoexcitations can generate a difference in photocurrent in perovskite solar cells due to the different SOC. The transient absorption and PL lifetime studies suggest the necessary conditions for generation of polarization dependent photocurrent and polarization dependent photoluminescence. When the spin lifetime is longer than charge dissociation time, the polarization dependent photocurrent can be observed in metal halide perovskites. When the spin lifetime is comparable to PL lifetime, polarization dependent photoluminescence can be realized. These findings provide fundamental understanding on optically tuning of spin-dependent dissociation and recombination processes in perovskites. Furthermore, the photoexcitation polarization dependent photocurrent and photoluminescence can be utilized as experimental tools to probe SOC, which have a great influence on optoelectronic properties of perovskites.

Chapter 5 Dipole Moment Effect on Light Emission Properties in Metal Halide Perovskite Nanoparticles

5.1 Abstract

Metal halide perovskite nanoparticles have attracted considerable attention as light emitters due to their narrow spectral width, tunable emission color, and high photoluminescence quantum efficiency. However, the conversion from bright state to dark state due to spin-orbital coupling (SOC) can give rise to additional non-radiative loss and limit light emission efficiency. In this work, we fabricate FAPbBr_3 nanoparticles with formamidinium (FA) cations partially substituted by near-zero dipole moment guanidinium (GUA) cations. By analyzing photoexcitation polarization dependent photoluminescence, lowered orbit-orbit interaction between photo-generated exciton in GUA doped perovskite nanoparticles can be observed. Improved photoluminescence quantum efficiency of 84% is achieved in GUA doped nanoparticles due to the suppressed conversion from bright state to dark state through SOC. The photoluminescence decay profiles, and photoluminescence anisotropy decay profiles suggest that the reduced SOC are induced by weakened orbit momentum associated with lowered electric polarization under photoexcitation in GUA doped nanoparticles. Our work provides new insight on improving the light emission efficiency of perovskite nanoparticles by considering electric polarization effects on SOC.

5.2 Introduction

Metal halide perovskites (MHPs) (with structure ABX_3 , where $\text{A}=\text{Cs}^+, \text{FA}^+, \text{MA}^+$; $\text{B}=\text{Pb}^{2+}, \text{Sn}^{2+}$; $\text{X}=\text{Br}^-, \text{I}^-, \text{Cl}^-$) have recently emerged as promising light emitting materials for light emitting diodes⁵⁵⁻⁵⁷ and lasers applications^{62, 63, 153}, due to the narrow spectral width^{154, 155}, tunable emission color^{156, 157}, high carrier mobility¹⁵⁸⁻¹⁶⁰, and low materials cost. In the past four years, the photoluminescence quantum yield of hybrid perovskites has been increased to near unity, while the external quantum efficiency of perovskite-based LEDs has been increased from 0.125% to over 20%^{66, 161, 162}. Different structure and composition engineering approaches, including mixed cations, quasi-2D structure^{69, 163, 164}, nanocrystal engineering¹⁶⁵⁻¹⁶⁷, have been reported to show improved light emission properties through improving crystallinity, passivating trap states, and enhancing exciton confinement. In 2018, Becker et al. demonstrated that CsPbX_3 ($\text{X}=\text{Br}, \text{I}, \text{Cl}$) nanocrystals have highly emissive triplet states based on theoretical and experimental analysis⁸⁹. The fine structure of band edge excitons in CsPbX_3 ($\text{X}=\text{Br}, \text{I}, \text{Cl}$) nanocrystals have recombination allowed triplet states, and recombination forbidden singlet state, under the influence of Rashba

effect and strong spin-orbital coupling (SOC). In this light, SOC and Rashba effect should be considered as important parameters in further improving the light emitting efficiency of perovskites. Early studies have shown that SOC in perovskites can be effectively tuned by substituting metal cation Pb with Sn or Ge^{168, 169}. Despite of emission color tuning, changing halide composition is also reported to have influence on SOC^{170, 171}. However, A site cations substitution is mostly studied for its effects on increasing crystallinity^{172, 173}, reducing trap density^{174, 175}, and improving thermo/moisture stability^{175, 176}. The possible influence on SOC induced by A-site cations substitution is barely addressed. It is known that the hybrid perovskites possess both orbital momenta ($\mathbf{L}$) and spin momentum ($\mathbf{S}$) with the total momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$ under influence of strong SOC⁸². Changing A site cation with different dipole moments can lead to a change in interaction between A-site cation and PbX₆ octahedra, resulting in a change of electric polarization. The change of electric polarization can influence the orbital momentum of excitons in perovskites and consequently influences SOC.

Here, the dipole moment effects on light emission properties of perovskite nanoparticles have been studied. Guanidinium (GUA) with zero dipole moment is introduced^{177, 178}, to partially substitute Formamidinium (FA) (dipole moment ~0.2D) in FAPbBr₃ nanoparticles. The orbit-orbit interaction between photogenerated excitons in both doped and undoped perovskite nanoparticles are examined by using polarized light modulated photoluminescence. A decrease of SOC can be determined in GUA doped nanoparticles, which is induced by the reduced orbit contribution associated with reduced electric polarization. Due to the suppressed bright-to-dark states conversion, improved light emission efficiency is obtained from FAPbBr₃ nanoparticles with GUA doping. Further, PL lifetime and PL anisotropy decay are studied to explore the possible mechanism of suppressing electric polarization with GUA doping. This chapter provides new insight on improving light emission properties of low dimensional perovskites by considering dipole moment effects on photoluminescence quantum efficiency through A-site cation doping.

5.3 Materials and Methods

5.3.1 Device fabrication

FAPbBr₃ nanoparticles were synthesized by using an emulsion system with two immiscible solvents (n,n-dimethylformamidinium (DMF) and hexane). We dissolved 0.4 mmol of

$\text{CH}(\text{NH}_2)_2\text{Br}$ (Sigma-Aldrich) and 0.4 mmol of PbBr_2 (Dyesol) in 1 mL of DMF to form a precursor solution. In another vial, we mixed 6.05 μmol of amine ligand and 0.25 mL of oleic acid with 5 mL of hexane. Dropping 0.4 mL of precursor solution into ligand-dissolved hexane solution with vigorous stirring yielded a milky emulsion. Dropwise addition of 4 mL of tertbutanol into the emulsion solution caused crystallization of perovskite. Guanidinium (GUA) cation doped perovskite NPs with GUA: FA molar ratio of 1:9 were synthesized by using the same method.

The FAPbBr_3 nanoparticles based light emitting diode are fabricated with device structure of ITO/PEDOT: PSS/ FAPbBr_3 /TPBI/LiF/Al (**Figure 5-1a**). The energy level diagram of the device is shown in **Figure 5-1b**. ITO patterned glasses were cleaned by sonication in acetone and 2-isopropanol for 15 min sequentially, and then boiled in 2-Isopropanol for 30 min. The glasses were dried, then UV-ozone was treated for 10 min. After UV-ozone treatment, PEDOT: PSS was spin-coated on the ITO patterned glasses at 4500 rpm for 90 s, then baked at 150 °C for 30 min. The substrates were transferred to a glove box and FAPbBr_3 NP solutions were spin-coated at 3000 rpm for 90 s. They were then baked at 90 °C for 10 min, then loaded in a vacuum chamber ($<10^{-7}$ Torr). Then, TPBI (50 nm) was deposited at 1 Å/s, LiF (1 nm) was deposited at 0.1 Å/s, and Al (100 nm) was deposited at 3 Å/s sequentially.

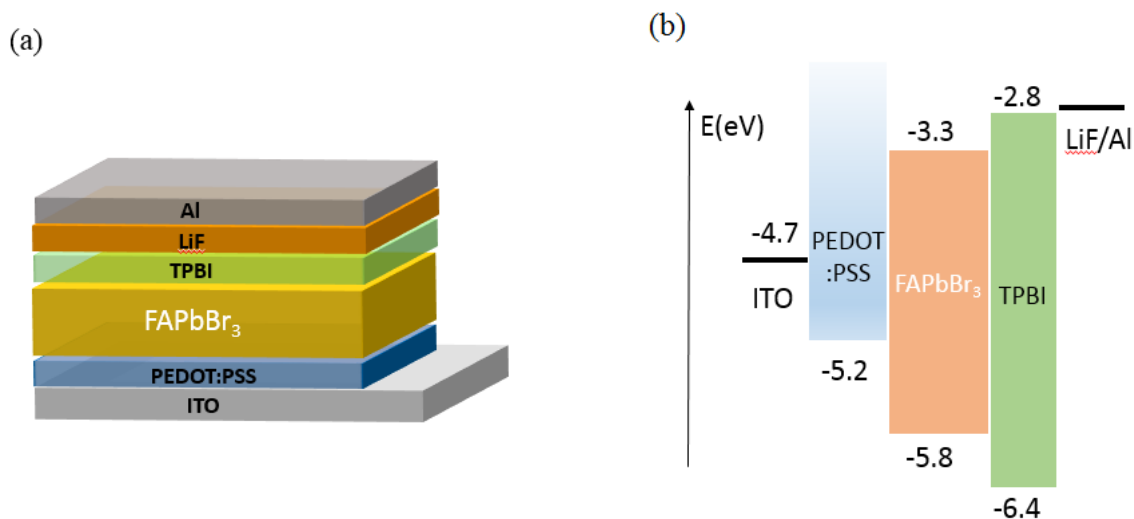


Figure 5- 1 (a) schematic diagram of perovskite light emitting diode. (b) Energy level diagram of perovskite light emitting diode.

5.3.2 Measurement and characterization

The photoluminescence and electroluminescence measurements were performed by Horiba Jobin Yvon Fluorolog-3 spectrometer. The photoexcitation was provided from a 405nm CW laser. For the photoexcitation polarization-dependent PL measurement, the linearly polarized laser beam with 2 mm diameter was combined with a $\frac{1}{4}$ wave plate to generate switchable linearly and circularly polarized photoexcitations with identical intensity when the $\frac{1}{4}$ wave plate was rotated with 0° and 45° relative to the direction of linear polarization of laser beam. The measurement setup can be referred to **Figure 4.2**. The PL decay time was measured by using Horiba Jobin Yvon Fluorolog-3 and Fluorohub. A nano-laser with 370nm excitation wavelength and 1 MHz repetition rate was used as excitation source. PLQEs of perovskite NP solutions were measured using the same spectrofluorometer with a 100-nm integrating sphere (ILF-835) and Jasco SpectraManager II Software. The excitation wavelength for measuring PLQEs was 375 nm.

Photoluminescence anisotropy decay measurement: Anisotropy decay measurements are performed with Horiba Jobin Yvon Fluorolog-3 and Fluorohub. 370nm nano-laser combined with a linear polarizer is used as plane-polarized excitation light. The photoluminescence emission is then detected through a second polarizer. The excitation source, sample and detection part are aligned in an “L geometry” (as shown in **Figure 5-2**). The time-resolved anisotropy $r(t)$ is

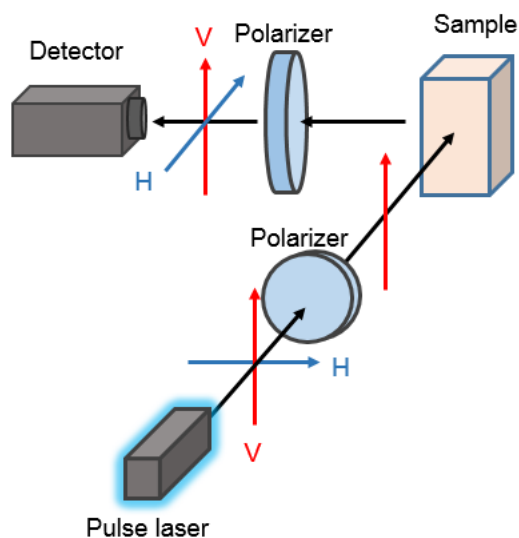


Figure 5- 2 Time-resolved photoluminescence anisotropy measurement setup.

calculated by:

$$r(t) = \frac{I_{VV}(t) - GI_{VH}(t)}{I_{VV}(t) + 2GI_{VH}(t)} \quad (5-1)$$

where $I_{VV}(t)$ is the intensity with vertically polarized excitation and vertical polarization on the detected emission. $I_{VH}(t)$ is the intensity with vertically polarized excitation and horizontal polarization on the detected emission. G is a wavelength-dependent grating factor used to correct the instrument's differential transmission of the two orthogonal vector orientations. It can be calculated by $G = \frac{I_{HV}}{I_{HH}}$, where $I_{HV}(t)$ is the intensity with horizontally polarized excitation and vertical polarization on the detected emission. $I_{HH}(t)$ is the intensity with horizontally polarized excitation and horizontal polarization on the detected emission.

5.4 Results and Discussion

The particle size distribution of FAPbBr₃ nanoparticles was determined by using transmission electron microscopy (**Figure 5-3a**). FAPbBr₃ nanoparticles were characterized of 10nm average particle size and a narrow particle size distribution, indicating a controlled crystallization kinetic for nanoparticles with emulsion method. However, perovskite nanoparticles with 10% GUA doping had smaller average size of 8nm. The decrease in particle size suggests that GUA cation doping can effectively influence crystallinity perovskite nanoparticles, preventing formation of larger crystals. Photoluminescence spectrums of undoped and GUA doped perovskite nanoparticles are shown in **Figure 5-3b**. PL spectrum of FAPbBr₃ nanoparticles was centered at 533nm with narrow spectrum width (~22nm). PL peak of GUA doped perovskite nanoparticles showed slightly blue shift at 532nm. The absorption spectrums were measured from FAPbBr₃ nanoparticles thin film samples (as shown in **Figure 5-3c**). The absorption spectrums for both GUA doped and undoped FAPbBr₃ nanoparticles were almost identical with absorption onsets around 527nm.

To explore GUA doping effects on light-emitting properties of FAPbBr₃ nanoparticles, linear/circular photoexcitation modulated photoluminescence measurement in probing bright-to-dark states conversion process was conducted. It has been studied that under the influence of strong SOC due to heavy Pb atom and electron-hole exchange interaction, the fine structure of band edge excitons in perovskite nanocrystals have recombination allowed J triplet states, and recombination

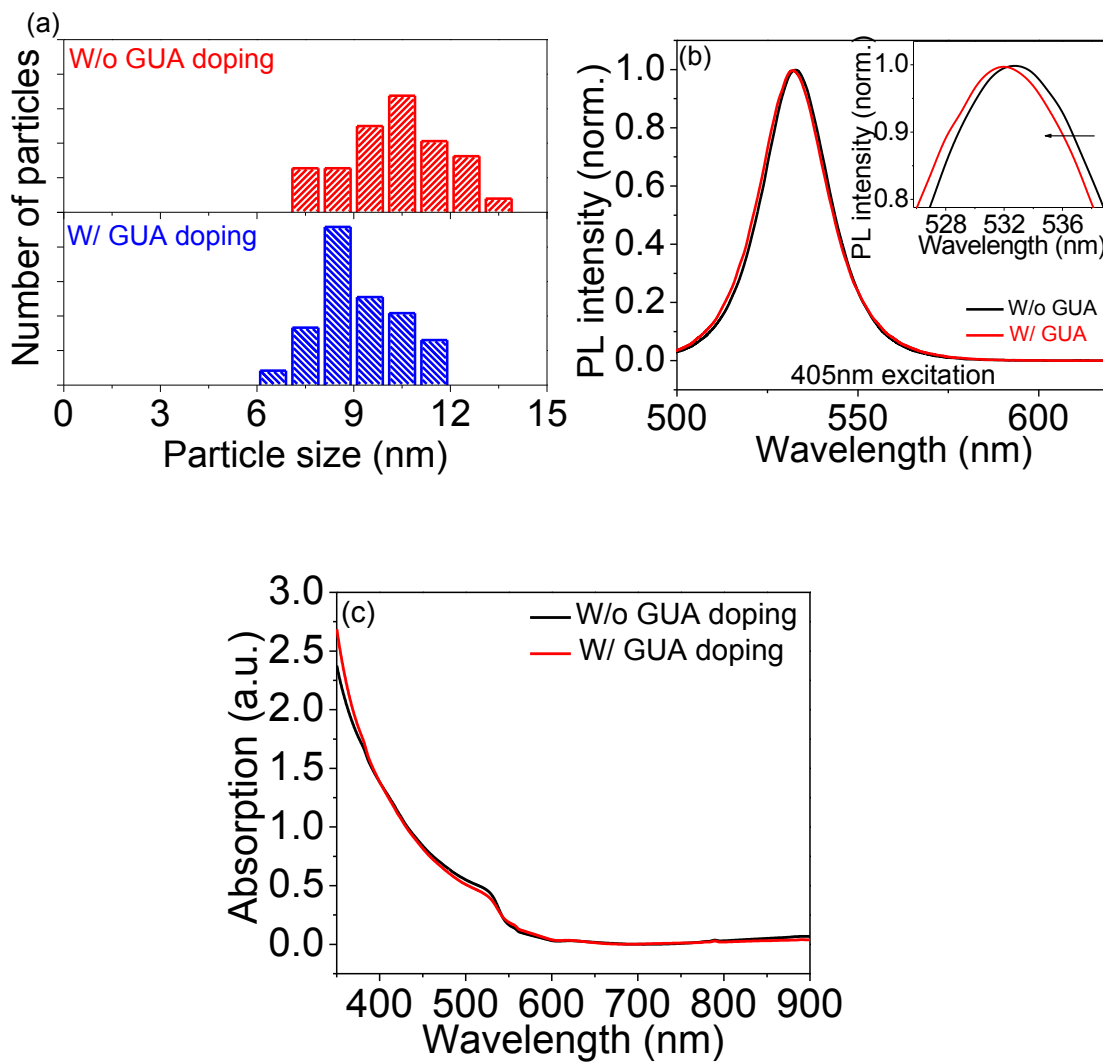


Figure 5- 3 (a) Photoluminescence spectrum of undoped and GUA doped FAPbBr₃ nanoparticle thin films. (b) FAPbBr₃ nanoparticle size with different GUA doping concentration.

forbidden J singlet state, namely, bright states and dark states. Under photoexcitation, excitons are formed with J triplet states in perovskites due to angular momentum conservation. SOC can serve as spin mixing that converts photo-generated bright excitons into dark excitons. Therefore, bright-to-dark state conversion is essentially a critical process that determining the photoluminescence efficiency of perovskite nanoparticles. In linear/circular photoexcitation modulated photoluminescence measurement, the photoluminescence intensity of FAPbBr₃ nanoparticles was monitored while photoexcitation was switched between linear and circular polarization by using the same optical path as shown in **Figure 4-2**. The experiment detail has been described in Chapter 4.3.3. It can be seen in **Figure 5-4a** that, PL intensity change with $\Delta PL=0.45\%$ can be observed from undoped FAPbBr₃ nanoparticles when 405nm photoexcitation was switched between linear and circular polarization with 100mW/cm² intensity. Meanwhile, ΔPL of 0.3% was obtained from GUA doped FAPbBr₃ nanoparticles as shown in **Figure 5-4b**. Here, ΔPL is defined by $\Delta PL = (I_{\text{Linear}} - I_{\text{Circular}}) / I_{\text{Circular}}$, where I_{Linear} and I_{Circular} are the PL intensities under linear and circular photoexcitations, respectively. In principle, left-hand (σ^+) or right-hand (σ^-) circularly polarized photoexcitation generates $J_z=+1$ or $J_z=-1$ excitons with same-directional orbital momentum. Whereas, linearly polarized photoexcitation can be considered as combination of left-hand and right-hand circular photoexcitation, generates both $J_z=+1$ and $J_z=-1$ excitons with opposite directional orbital momentum. It should be pointed out, when the orbitals encounter interaction through magnetic dipoles formed from orbital current loops, excitons with same-directional orbital momentums exhibit stronger total magnetic dipoles under circular photoexcitation. In contrast, excitons with opposite-directional orbital momentums formed under linear photoexcitation have weaker total magnetic dipoles. As a consequence, stronger and weaker SOC are generated under circular and linear photoexcitation through orbit-orbit interaction^{81, 179}. Importantly, bright excitons can convert into dark excitons due to orbit-orbit interaction through SOC. Thus, circular and linear photoexcitations generate stronger and weaker bright-to-dark state conversion leading to different populations of bright and dark states, consequently yield to different light emission intensity (**Figure 5-4c**).

It is worth noting that photoexcitation polarization dependent photoluminescence cannot be observed in perovskite nanoparticles below certain photoexcitation intensity. The threshold excitation intensity required to generate ΔPL for undoped FAPbBr₃ nanoparticles and GUA doped

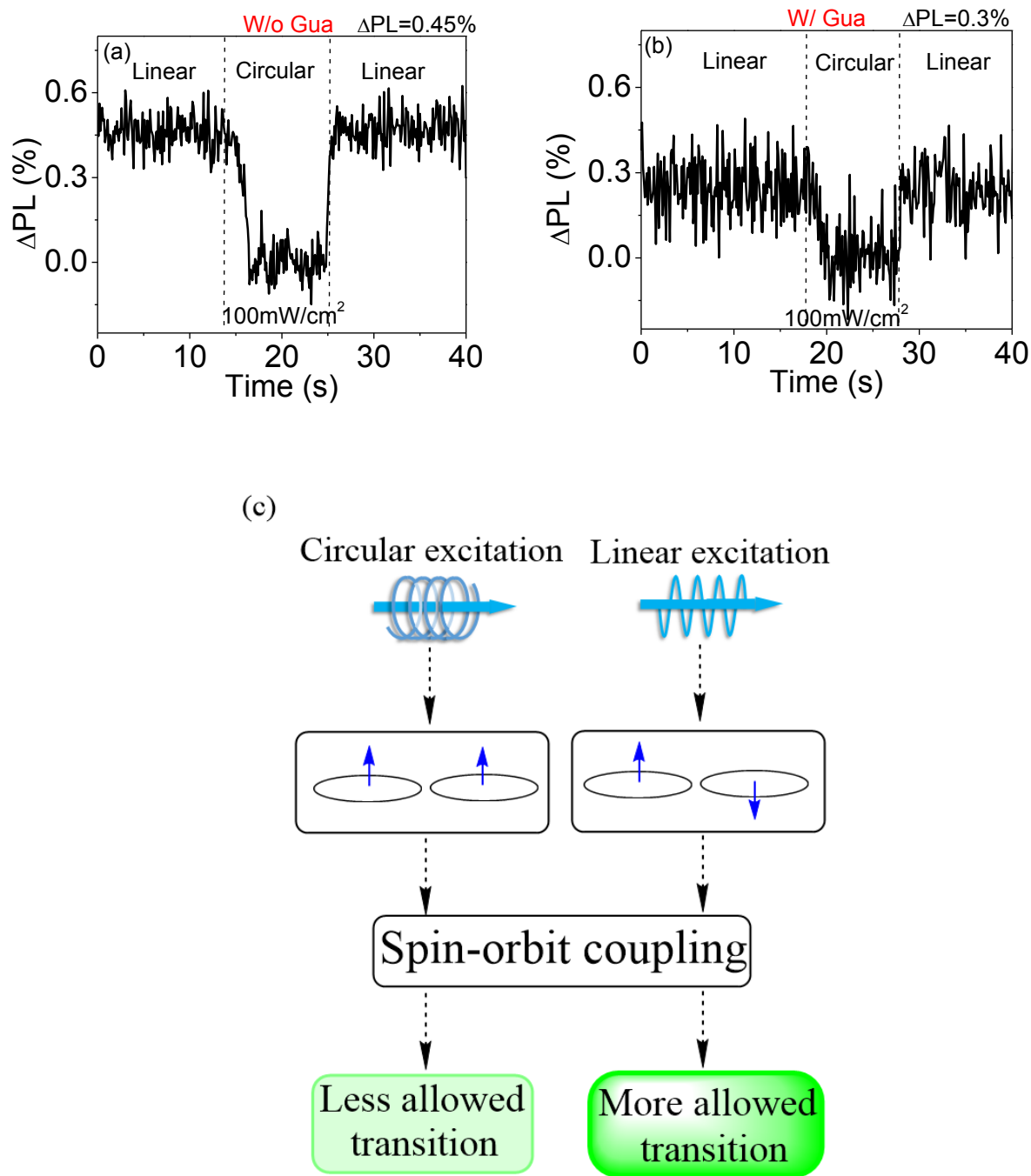


Figure 5- 4 (a) Polarization dependent photoluminescence of FAPbBr₃ nanoparticle thin film with 100 mW/cm^2 photoexcitation. (b) Polarization dependent photoluminescence of GUA doped FAPbBr₃ nanoparticle thin film with 100 mW/cm^2 photoexcitation. (c) Schematic diagram of linear/circular photoexcitation modulated photoluminescence in perovskites.

nanoparticles were 50mW/cm² and 100mW/cm², respectively (**Figure 5-5a**). It should be pointed out, the absorption intensities for both nanoparticle samples are almost identical at 488nm as shown in **Figure 5-3c**. Therefore, the different threshold excitation intensity for Δ PL caused by absorption difference can be excluded. Importantly, the realization of Δ PL relies on photoexcitation induced SOC change through orbit-orbit interaction between excitons. When the orbit-orbit interaction between excitons is relatively weak, no difference in spin-mixing can be induced between linear and circular photo-generated excitons, leading to a negligible change in PL intensity. By increasing photoexcitation intensity to a certain threshold value, the orbit-orbit interaction between excitons can be enhanced due to the increased density of excitons. Linear and circular photoexcitation generated excitons can experience different bright-to-dark state conversion process, leading to an appreciable change in PL intensity. Based on this analysis, threshold excitation intensity for polarization dependent photoluminescence can provide essential insight on intrinsic orbit-orbit interaction between excitons in different perovskites. Here, compared to undoped nanoparticles, higher threshold excitation intensity observed for GUA doped nanoparticles suggests that, excitons generated in GUA doped nanoparticles have weaker orbit-orbit interaction between each other, leading to weaker bright-to-dark state conversion. **Figure 5-5b** shows the PLQEs measured for both perovskite nanoparticles with and without GUA doping. GUA doped nanoparticles have an improved PLQE (~84%), comparing with undoped FAPbBr₃ nanoparticles (~69%). This result can be attributed to the weaker bright-to-dark state conversion process in GUA doped nanoparticles. Theoretically, the hybrid metal halide perovskites possess both orbital momentum (**L**) and spin momentum (**S**) with the total momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$. The interaction between **J** polarized excitons generated by polarized light can be affected by both the orbital momentum and spin momentum through spin-orbital coupling. Changing electric polarized and magnetic polarization in perovskites can effectively change orbital momentum and spin momentum, respectively. Electric polarization of perovskite nanoparticles can be possibly affected by GUA cation doping through: 1) passivating the charged defects at grain boundaries^{177, 180}, leading to a decrease in electric polarization, 2) substituting FA with near-zero dipole moment cation GUA, leading to a suppressed dielectric response under photoexcitation. In the former and later regime, the surface and bulk electric polarization can be reduced, respectively. Accordingly, orbit-orbit interaction between excitons becomes weaker in GUA doped nanoparticles based on the weaker SOC.

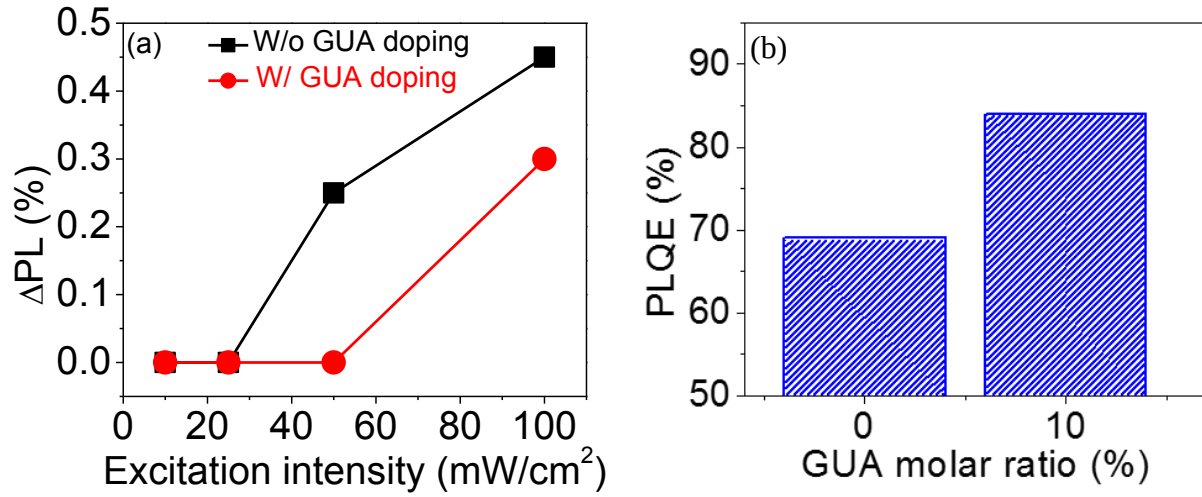


Figure 5- 5 (a) PL intensity change by switching photoexcitation polarization as a function of excitation intensity for GUA doped FAPbBr₃ nanoparticle thin films. (b) PLQE of undoped and 10% GUA doped FAPbBr₃ nanoparticle thin films.

To further confirm the relationship between orbit-orbit interaction and light emission efficiency in FAPbBr₃ nanoparticles, PL lifetime was measured by using time-correlated single-photon counting (TCSPC) system. PL decay curve of FAPbBr₃ nanoparticles was fitted with a two-exponential equation:

$$I(t) = \alpha_1 e^{-t/\tau_1} + \alpha_2 e^{-t/\tau_2} \quad (5-1)$$

where τ_1 and τ_2 are the time constant of PL decay component 1 and PL decay component 2, α_1 and α_2 are the intensity contributions of component 1 and component 2 to PL decay, respectively. It can be seen that the PL decay curves represent a fast component and a slow component (**Table 5-1**). Generally, the fast component of PL decay is related to the trap-assisted recombination of photo-generated carriers at the surface of nanoparticles and grain boundaries. The slow component refers to the radiative recombination of geminate electron-hole pairs inside the nanoparticles^{66, 167}. The undoped FAPbBr₃ nanoparticles showed slightly shorter PL lifetime and higher fraction of short PL decay component ($\alpha_1 \sim 19.8\%$) than GUA doped nanoparticles ($\alpha_1 \sim 17.6\%$) (**Figure 5-6a**).

Table 5-1. PL lifetime of FAPbBr₃ nanoparticles and GUA doped FAPbBr₃ nanoparticles.

	τ_1 (ns)	α_1 (%)	τ_2 (ns)	α_2 (%)
0% GUA	11	19.8	151	80.2
10% GUA	13	17.6	152	82.4

It is known that most nanoparticles contain under-coordinated ions at particle surface and grain boundaries between crystals. GUA molecules are likely to reside at grain boundaries to form hydrogen bonds with under-coordinated bromide ions due to its strong hydrogen bonds formation capacity. Consequently, the charge trapping species at surface of FAPbBr₃ nanoparticles can be passivated by GUA doping. However, the relatively small change in PL lifetime suggests that the improved light emitting efficiency upon GUA doping is not mainly contributed from the suppression of trap assisted non-radiative recombination. It is also important to note that, the surface polarization of nanoparticle cannot be readily tuned by GUA doping, due to the inefficiency surface trap passivation.

To get further understanding on the weakening of SOC upon GUA doping, we measured photoluminescence anisotropy decay. It has been studied bulk polycrystalline hybrid perovskites can exhibit polarization memory due to the anisotropic crystal structure and polar distortion of local crystal lattice¹⁸¹⁻¹⁸⁴. Based on this, linear photoexcitation generated excited states in hybrid perovskite can maintain the initial polarization anisotropy with certain timescale. It can be seen in **Figure 5-6b**, the photoluminescence anisotropy for undoped FAPbBr₃ nanoparticles was measured to decay within 10ns. Whereas, GUA doped FAPbBr₃ nanoparticles did not exhibit a detectable photoluminescence anisotropy within our detection limit (**Figure 5-6c**). We should note that FAPbBr₃ nanoparticles have cubic crystal structure which cannot be responsible for maintaining polarization anisotropy. However, polar distortion of local crystal lattice can be induced due to the rotation of polar cation FA⁺ under photoexcitation, leading to larger bulk polarization¹⁸⁵. Partially substituting FA with GUA can effectively reduce polar distortion generated from rotational organic cations, and consequently leads to weaker bulk polarization. Clearly, the negligible PL anisotropy of GUA doped perovskite nanoparticles indicates a relatively

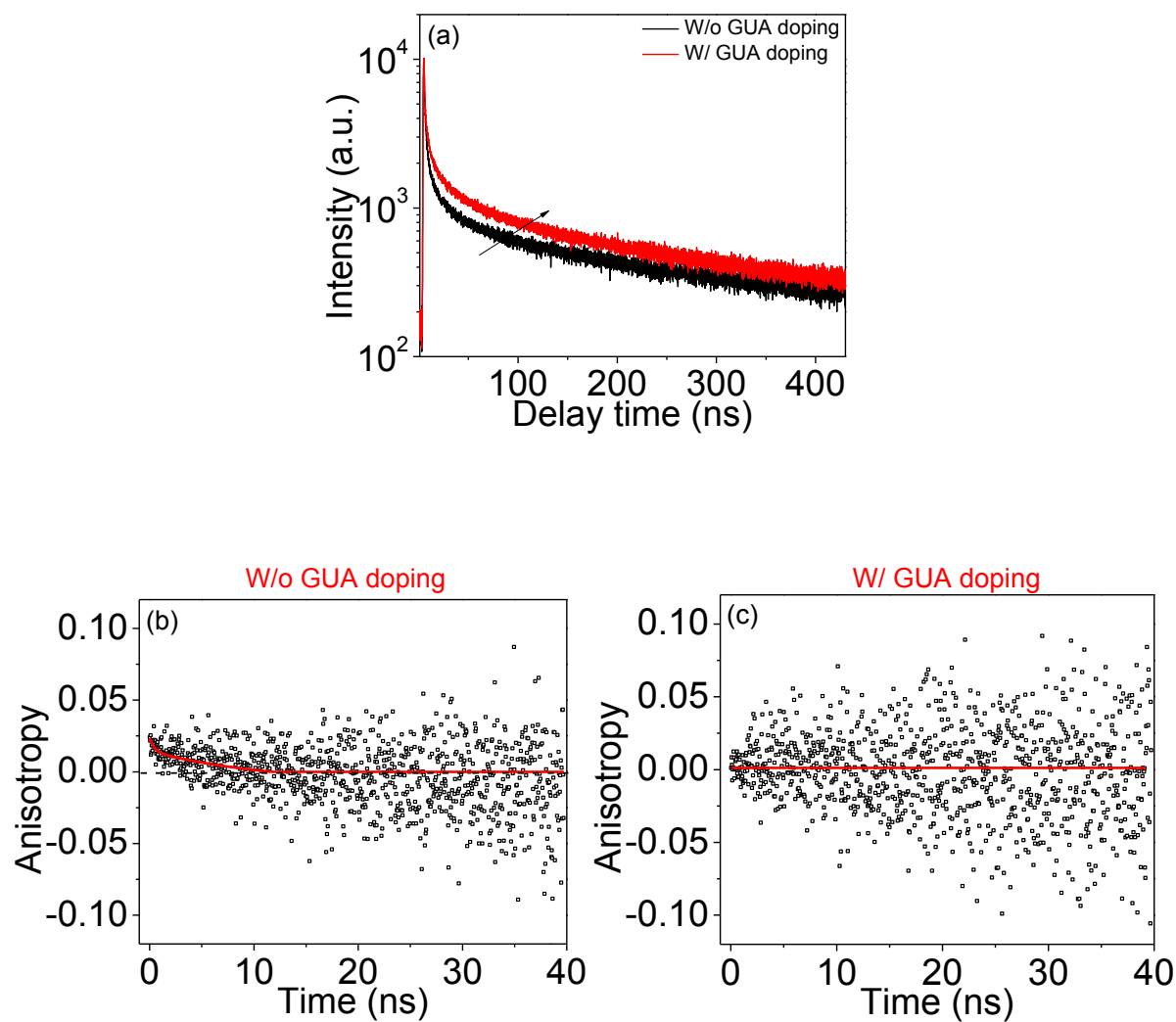


Figure 5- 6 (a) PL lifetime of undoped and GUA doped FAPbBr₃ nanoparticles. (b) PL anisotropy decay of FAPbBr₃ nanoparticles, (c) PL anisotropy decay of GUA doped FAPbBr₃ nanoparticles.

weak bulk electric polarization. Consequently, GUA doped perovskite nanoparticles possess weaker SOC due to the suppressed electric polarization.

The EL characteristics and device efficiencies were measured in undoped FAPbBr₃ nanoparticles and GUA doped perovskite nanoparticle LEDs with device structure of ITO/ PEDOT: PSS/MHP NPs/TPBI/LiF/Al. Similar to the PL spectrum, a blue shift in EL spectrum was observed for GUA doped nanoparticle LED, which was attributed to enhanced quantum confinement of electron-hole pairs generated from charge injection (**Figure 5-7a**). In every applied bias, GUA doped nanoparticles LED showed enhanced luminance compared to undoped FAPbBr₃ nanoparticles LED (**Figure 5-7b**). An improved luminescence efficiency 16830cd/m² was achieved in GUA doped nanoparticle LED, as compared to the undoped FAPbBr₃ nanoparticle LED (4260cd/m²). The improved device performance can be attributed to 1) improved PLQE of nanoparticles with weaker bright-to-dark states conversion due to SOC, 2) improved charge injection and transport in nanoparticles due to improved film continuity. However, further increasing GUA: FA molar ratio above 10%, device performance began to decrease. This result suggests that charge injection and transport can be impeded in nanoparticles with reduced size and higher surface to volume ratio^{67, 186}.

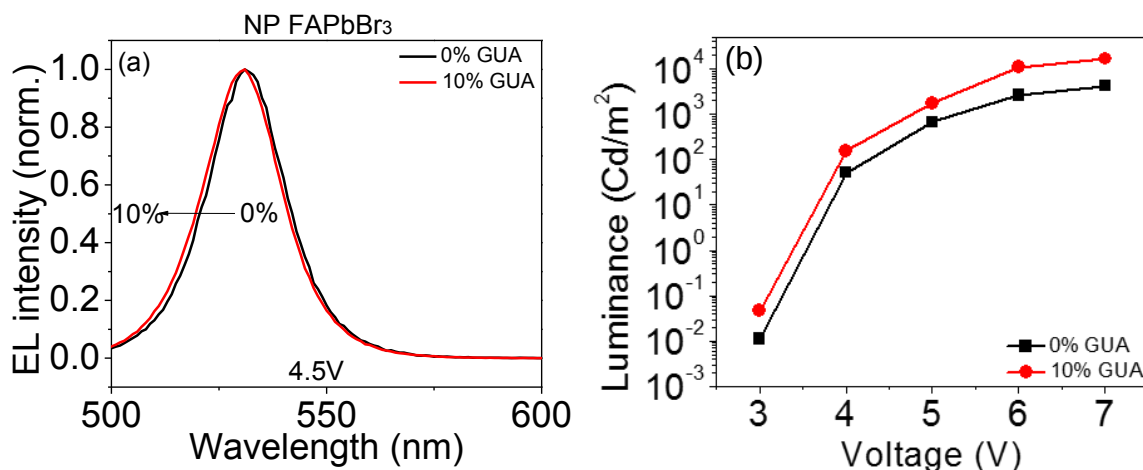


Figure 5- 7 (a) Electroluminescence spectrum of FAPbBr₃ nanoparticle LEDs with different GUA dopant concentration. (b) Luminance characteristics of FAPbBr₃ nanoparticle LEDs.

5.5 Summary

In sum, FAPbBr₃ nanoparticles and nanoparticles with proper amount GUA cation doping were synthesized. The dipole moment effect from GUA doping on light emission properties is studied. The linear/circular photoexcitation modulated photoluminescence measurements indicate that zero dipole moment cation GUA doping in FAPbBr₃ nanoparticles can lead to suppressed bright-to-dark state conversion process in excitons due to the weaker orbit-orbit interaction. Accordingly, PLQE of FAPbBr₃ nanoparticles increases from 69% to 84% with 10% molar ratio GUA doped. PL lifetime characteristics suggest that, the improvement in photoluminescence quantum efficiency should not be attributed to the insignificant trap passivation due to GUA doping. The PL anisotropy decay measurement confirms that GUA doping can essentially weaken the electric polarization in perovskite nanoparticles, leading to a weaker SOC, and consequently suppresses bright-to-dark state conversion. An improved luminescence of 16830cd/m² is achieved in GUA doped nanoparticle LED. Our results suggest that reducing electric polarization in perovskite nanoparticles through GUA cation doping can be a promising approach to further improve light emitting properties of perovskite NPs.

Chapter 6 Conclusion

The magnetic-optical effects in multifunctional materials and newly emerging metal halide perovskites are studied in this research. Magnetic field effects are applied as an effective tool to study the spin and polarization-dependent behavior of multi-functional materials in excited states. Also, new magneto-optical effects are explored to analyze the internal coupling between magnetic and optical properties in multi-functional materials.

First, we experimentally studied magneto-photoluminescence by using two-photon and three-photon excitations based on the $\text{Y}_2\text{O}_3\text{S: Er, Yb}$ and $\text{NaYF}_4\text{: Tm, Yb}$ particles. The magneto-photoluminescence can be observed above certain threshold excitation intensity. We proposed the possible mechanism of this photoexcitation intensity dependent magneto-photoluminescence by considering spin-dependent transition dipoles. When the photoexcitation exceeds the critical intensity, the exchange interaction between electric dipoles becomes weak due to Coulomb screening effects, allowing spin mixing induced by SOC to happen. An external magnetic field can then disturb the equilibrium established by the competition between exchange interaction and SOC, modifying the populations on antiparallel and parallel dipoles, leading to an appreciable magneto-photoluminescence. Based on this analysis, we further studied the magneto-photoluminescence through down-conversion and three photon up-conversion. By comparing the curve-shape of the magnetic field effects, the key parameter and process to generate magneto-photoluminescence in up-conversion crystals are revealed. These findings provide new insight to generate magneto-optical effects in up-conversion materials by considering the spin-dependent electric dipoles, and potential of field sensing and IR detection application based on up-conversion materials.

Second, a new steady state pump-probe measurement in magnetic field was developed for studying magnetic properties of nanoparticles suspension in both ground state and excited states. By using magnetic field effect of light scattering, a stronger magnetic response and faster response time were observed in MNP-graphene hybrid than in pristine graphene. More importantly, the amplitude of MFE of scattering from the hybrid sample can be enhanced upon applying excitation beam, which indicates that photoexcitation can induce enhanced magnetization due to the interaction between delocalized π electrons and localized spins in graphene. In addition, the ligand effect on the coupling between MNP and graphene is studied with MFE of light scattering. The result suggests that mediated non-covalent assembly of MNPs on to graphene through ligands in

the nanohybrid MYG can lead to enhanced anisotropic magnetism. Our study reveals fundamental information about the internal coupled magnetic and semiconducting properties in dedicated designed MNP-graphene nanohybrid. Also, the optically tunable magnetic properties in 0D-2D heterostructure give rise to new possibilities to design magnetic imaging and displays.

Last, the SOC effects on charge recombination and dissociation process in newly emerged metal halide perovskites have been studied. With strong SOC modulated band structure, electron-hole pairs with different orbit fields can be generated with polarized photoexcitation. By analyzing the curve-shape of magneto-photoluminescence, we found that the interaction between the same directional and opposite directional orbit momentums can give rise to optically tunable SOC, and consequently generating photovoltaic actions. Our study indicates that the in presence of orbit field, the conversion between bright and dark states through SOC can be detected in perovskites, leading to a photoexcitation dependent SOC. Moreover, the polarized photoexcitations dependent photocurrent and photoluminescence can be used as effective tools to explore the SOC and Rashba effects in perovskites. Based on this understanding, we studied the dipole moment effect on SOC as well as light emission properties of SOC in perovskite upon GUA doping. The photoexcitation polarization dependent photoluminescence suggests that SOC is reduced in GUA doped perovskite due to the reduced electric polarization. As a consequence, the conversion from bright to dark state is effectively suppressed, leading to an improved photoluminescence quantum efficiency. This series of studies provide insightful understanding on the nature of SOC mediated recombination and dissociation process of electron-hole pairs in perovskite. It also provides an important guideline for designing metal-halide perovskite by considering the SOC.

In sum, this thesis provides both fundamental understand and future possibilities for magneto-optical effects in multi-functional materials.

Reference

1. R. P. Groff, R. E. Merrifield, A. Suna and P. Avakian, *Phys. Rev. Lett.*, 1972, **29**, 429-431.
2. V. Ern and R. E. Merrifield, *Phys. Rev. Lett.*, 1968, **21**, 609-611.
3. R. Merrifield, *The Journal of Chemical Physics*, 1968, **48**, 4318-4319.
4. V. Dediu, M. Murgia, F. Maticcotta, C. Taliani and S. Barbanera, *Solid State Commun.*, 2002, **122**, 181-184.
5. B. Hu and Y. Wu, *Nat. Mater.*, 2007, **6**, 985.
6. T. D. Nguyen, H. M. Golda, F. J. Wang, L. Wojcik, X. G. Li, E. Ehrenfreund and Z. V. Vardeny, *Nat. Mater.*, 2010, **9**, 345.
7. T. D. Nguyen, B. R. Gautam, E. Ehrenfreund and Z. V. Vardeny, *Phys. Rev. Lett.*, 2010, **105**, 166804.
8. T. D. Nguyen, Y. Sheng, J. Rybicki and M. Wohlgenannt, *Phys. Rev. B*, 2008, **77**, 235209.
9. T. D. Nguyen, Y. Sheng, M. Wohlgenannt and T. D. Anthopoulos, *Synth. Met.*, 2007, **157**, 930.
10. T. D. Nguyen, Y. Sheng, J. Rybicki, G. Veeraraghavan and M. Wohlgenannt, *J. Mater. Chem.*, 2007, **17**, 1995.
11. P. A. Bobbert, T. D. Nguyen, F. W. A. van Oost, B. Koopmans and M. Wohlgenannt, *Phys. Rev. Lett.*, 2007, **99**, 216801.
12. F. L. Bloom, W. Wagemans, M. Kemerink and B. Koopmans, *Phys. Rev. Lett.*, 2007, **99**, 257201.
13. W. Wagemans, F. L. Bloom, P. A. Bobbert, M. Wohlgenannt and B. Koopmans, *J. Appl. Phys.*, 2008, **103**, 07F303.
14. L. Yan, M. Wang, N. P. Raju, A. Epstein, L.-S. Tan, A. Urbas, L. Y. Chiang and B. Hu, *J. Am. Chem. Soc.*, 2012, **134**, 3549-3554.
15. Z. Xu and B. Hu, *Adv. Funct. Mater.*, 2008, **18**, 2611-2617.
16. Y. Wu, Z. Xu, B. Hu and J. Howe, *Phys. Rev. B*, 2007, **75**, 035214.

17. F. Bloom, M. Kemerink, W. Wagemans and B. Koopmans, *Phys. Rev. Lett.*, 2009, **103**, 066601.
18. F. Wang, H. Bässler and Z. V. Vardeny, *Phys. Rev. Lett.*, 2008, **101**, 236805.
19. J. Bergeson, V. Prigodin, D. Lincoln and A. Epstein, *Phys. Rev. Lett.*, 2008, **100**, 067201.
20. P. Desai, P. Shakya, T. Kreouzis, W. Gillin, N. Morley and M. Gibbs, *Phys. Rev. B*, 2007, **75**, 094423.
21. L. He, M. Li, A. Urbas and B. Hu, *Phys. Rev. B*, 2014, **89**, 155304.
22. J. Kalinowski, M. Cocchi, D. Virgili, P. Di Marco and V. Fattori, *Chem. Phys. Lett.*, 2003, **380**, 710-715.
23. Ö. Mermer, G. Veeraraghavan, T. Francis, Y. Sheng, D. Nguyen, M. Wohlgenannt, A. Köhler, M. K. Al-Suti and M. Khan, *Phys. Rev. B*, 2005, **72**, 205202.
24. E. Frankevich, A. Lymarev, I. Sokolik, F. Karasz, S. Blumstengel, R. Baughman and H. Hörhold, *Phys. Rev. B*, 1992, **46**, 9320.
25. H. Zang, L. Yan, M. Li, L. He, Z. Gai, I. Ivanov, M. Wang, L. Chiang, A. Urbas and B. Hu, *Sci. Rep.*, 2013, **3**.
26. L. He, M. Li, H. Xu and B. Hu, *Nanoscale*, 2017, **9**, 2563-2568.
27. L. J. Rothberg and A. J. Lovinger, *J. Mater. Res.*, 1996, **11**, 3174-3187.
28. Y. Wu, B. Hu, J. Howe, A.-P. Li and J. Shen, *Phys. Rev. B*, 2007, **75**, 075413.
29. M. A. Baldo, C. Adachi and S. R. Forrest, *Phys. Rev. B*, 2000, **62**, 10967-10977.
30. R. Liu, Y. Zhang, Y. L. Lei, P. Chen and Z. H. Xiong, *J. Appl. Phys.*, 2009, **105**, 093719.
31. H. Tachikawa and A. J. Bard, *Chem. Phys. Lett.*, 1974, **26**, 246-251.
32. P. Desai, P. Shakya, T. Kreouzis and W. P. Gillin, *Phys. Rev. B*, 2007, **76**, 235202.
33. V. Dyakonov, G. Zorinians, M. Scharber, C. J. Brabec, R. A. J. Janssen, J. C. Hummelen and N. S. Sariciftci, *Phys. Rev. B*, 1999, **59**, 8019-8025.
34. J. D. Ceuster, E. Goovaerts, A. Bouwen, J. C. Hummelen and V. Dyakonov, *Phys. Rev. B*, 2001, **64**, 195206.

35. I. V. Khudyakov, Y. A. Serebrennikov and N. J. Turro, *Chem. Rev.*, 1993, **93**, 537-570.
36. K. M. Salikhov, R. Z. Sagdeev and A. L. Buchachenko, *Spin polarization and magnetic effects in radical reactions*, Elsevier, Netherlands, 1984.
37. N. J. Turro, *Proceedings of the National Academy of Sciences*, 1983, **80**, 609-621.
38. E. L. Frankevich, A. A. Lymarev, I. Sokolik, F. E. Karasz, S. Blumstengel, R. H. Baughman and H. H. Hörhold, *Phys. Rev. B*, 1992, **46**, 9320-9324.
39. S. Bagnich, U. Niedermeier, C. Melzer, W. Sarfert and H. von Seggern, *J. Appl. Phys.*, 2009, **106**, 113702.
40. Z. Xu, Y. Wu and B. Hu, *Appl. Phys. Lett.*, 2006, **89**, 131116.
41. Y.-C. Hsiao, T. Wu, M. Li, W. Qin, L. Yu and B. Hu, *Nano Energy*, 2016, **26**, 595-602.
42. W. Chang, D. N. Congreve, E. Hontz, M. E. Bahlke, D. P. McMahon, S. Reineke, T. C. Wu, V. Bulović, T. Van Voorhis and M. A. Baldo, *Nat. Commun.*, 2015, **6**, 6415.
43. M. Wittmer and I. Zschokke-Gränacher, *The Journal of Chemical Physics*, 1975, **63**, 4187-4194.
44. W. Helfrich, *Phys. Rev. Lett.*, 1966, **16**, 401-403.
45. J. Levinson, S. Z. Weisz, A. Cobas and A. Rolón, *The Journal of Chemical Physics*, 1970, **52**, 2794-2795.
46. M. Pope, J. Burgos and N. Wotherspoon, *Chem. Phys. Lett.*, 1971, **12**, 140-143.
47. M. Schott and J. Berrehar, *Molecular Crystals and Liquid Crystals*, 1973, **20**, 13-25.
48. F. A. Erbacher, R. Lenke and G. Maret, *EPL (Europhysics Letters)*, 1993, **21**, 551.
49. J. Liu, E. M. Lawrence, A. Wu, M. L. Ivey, G. A. Flores, K. Javier, J. Bibette and J. Richard, *Phys. Rev. Lett.*, 1995, **74**, 2828-2831.
50. M. Ivey, J. Liu, Y. Zhu and S. Cutillas, *Physical Review E*, 2000, **63**, 011403.
51. F. Lin, Z. Zhu, X. Zhou, W. Qiu, C. Niu, J. Hu, K. Dahal, Y. Wang, Z. Zhao, Z. Ren, D. Litvinov, Z. Liu, Z. M. Wang and J. Bao, *Adv. Mater.*, 2017, **29**, 1604453-n/a.

52. H. Tan, A. Jain, O. Voznyy, X. Lan, F. P. G. de Arquer, J. Z. Fan, R. Quintero-Bermudez, M. Yuan, B. Zhang and Y. Zhao, *Science*, 2017, **355**, 722-726.
53. M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate and A. Hagfeldt, *Energy Environ. Sci.*, 2016, **9**, 1989-1997.
54. J. You, L. Meng, T.-B. Song, T.-F. Guo, Y. M. Yang, W.-H. Chang, Z. Hong, H. Chen, H. Zhou and Q. Chen, *Nat. Nanotechnol.*, 2016, **11**, 75.
55. H. Cho, S.-H. Jeong, M.-H. Park, Y.-H. Kim, C. Wolf, C.-L. Lee, J. H. Heo, A. Sadhanala, N. Myoung and S. Yoo, *Science*, 2015, **350**, 1222-1225.
56. Z.-K. Tan, R. S. Moghaddam, M. L. Lai, P. Docampo, R. Higler, F. Deschler, M. Price, A. Sadhanala, L. M. Pazos and D. Credgington, *Nat. Nanotechnol.*, 2014, **9**, 687-692.
57. Y. K. Chih, J. C. Wang, R. T. Yang, C. C. Liu, Y. C. Chang, Y. S. Fu, W. C. Lai, P. Chen, T. C. Wen and Y. C. Huang, *Adv. Mater.*, 2016, **28**, 8687-8694.
58. L. Dou, Y. M. Yang, J. You, Z. Hong, W.-H. Chang, G. Li and Y. Yang, *Nature communications*, 2014, **5**, 5404.
59. Y. Fang and J. Huang, *Adv. Mater.*, 2015, **27**, 2804-2810.
60. R. Dong, Y. Fang, J. Chae, J. Dai, Z. Xiao, Q. Dong, Y. Yuan, A. Centrone, X. C. Zeng and J. Huang, *Adv. Mater.*, 2015, **27**, 1912-1918.
61. G. Xing, N. Mathews, S. S. Lim, N. Yantara, X. Liu, D. Sabba, M. Grätzel, S. Mhaisalkar and T. C. Sum, *Nat. Mater.*, 2014, **13**, 476.
62. H. Zhu, Y. Fu, F. Meng, X. Wu, Z. Gong, Q. Ding, M. V. Gustafsson, M. T. Trinh, S. Jin and X. Zhu, *Nat. Mater.*, 2015, **14**, 636.
63. F. Deschler, M. Price, S. Pathak, L. E. Klintberg, D.-D. Jarausch, R. Higler, S. Hüttner, T. Leijtens, S. D. Stranks and H. J. Snaith, *J. Phys. Chem. Lett.*, 2014, **5**, 1421-1426.
64. A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *J. Am. Chem. Soc.*, 2009, **131**, 6050-6051.

65. Q. Jiang, Y. Zhao, X. Zhang, X. Yang, Y. Chen, Z. Chu, Q. Ye, X. Li, Z. Yin and J. You, *Nat. Photonics*, 2019, **13**, 460-466.
66. Y. H. Kim, H. Cho, J. H. Heo, T. S. Kim, N. Myoung, C. L. Lee, S. H. Im and T. W. Lee, *Adv. Mater.*, 2015, **27**, 1248-1254.
67. Z. Xiao, R. A. Kerner, L. Zhao, N. L. Tran, K. M. Lee, T.-W. Koh, G. D. Scholes and B. P. Rand, *Nat. Photonics*, 2017, **11**, 108.
68. Y. Fu, H. Zhu, C. C. Stoumpos, Q. Ding, J. Wang, M. G. Kanatzidis, X. Zhu and S. Jin, *ACS nano*, 2016, **10**, 7963-7972.
69. M. Yuan, L. N. Quan, R. Comin, G. Walters, R. Sabatini, O. Voznyy, S. Hoogland, Y. Zhao, E. M. Beauregard, P. Kanjanaboos, Z. Lu, D. H. Kim and E. H. Sargent, *Nat. Nanotechnol.*, 2016, **11**, 872.
70. L. N. Quan, Y. Zhao, F. P. García de Arquer, R. Sabatini, G. Walters, O. Voznyy, R. Comin, Y. Li, J. Z. Fan, H. Tan, J. Pan, M. Yuan, O. M. Bakr, Z. Lu, D. H. Kim and E. H. Sargent, *Nano Lett.*, 2017, **17**, 3701-3709.
71. J. Byun, H. Cho, C. Wolf, M. Jang, A. Sadhanala, R. H. Friend, H. Yang and T. W. Lee, *Adv. Mater.*, 2016, **28**, 7515-7520.
72. Y. Wang, X. Li, J. Song, L. Xiao, H. Zeng and H. Sun, *Adv. Mater.*, 2015, **27**, 7101-7108.
73. H. Huang, A. S. Susha, S. V. Kershaw, T. F. Hung and A. L. Rogach, *Advanced Science*, 2015, **2**, 1500194.
74. Z. Li, L. Kong, S. Huang and L. Li, *Angewandte Chemie*, 2017, **129**, 8246-8250.
75. D. Giovanni, H. Ma, J. Chua, M. Grätzel, R. Ramesh, S. Mhaisalkar, N. Mathews and T. C. Sum, *Nano Lett.*, 2015, **15**, 1553-1558.
76. Y.-C. Hsiao, T. Wu, M. Li and B. Hu, *Adv. Mater.*, 2015, **27**, 2899-2906.
77. C. Zhang, D. Sun, C. Sheng, Y. Zhai, K. Mielczarek, A. Zakhidov and Z. Vardeny, *Nat. Phys.*, 2015, **11**, 427.

78. P. Odenthal, W. Talmadge, N. Gundlach, R. Wang, C. Zhang, D. Sun, Z.-G. Yu, Z. Vally Vardeny and Y. S. Li, *Nat. Phys.*, 2017, **13**, 894.
79. J. Wang, C. Zhang, H. Liu, R. McLaughlin, Y. Zhai, S. R. Vardeny, X. Liu, S. McGill, D. Semenov, H. Guo, R. Tsuchikawa, V. V. Deshpande, D. Sun and Z. V. Vardeny, *Nature Communications*, 2019, **10**, 129.
80. J. Zhang, T. Wu, J. Duan, M. Ahmadi, F. Jiang, Y. Zhou and B. Hu, *Nano energy*, 2017, **38**, 297-303.
81. W. Qin, H. Xu and B. Hu, *ACS Photonics*, 2017, **4**, 2821-2827.
82. M. Kim, J. Im, A. J. Freeman, J. Ihm and H. Jin, *Proceedings of the National Academy of Sciences*, 2014, 201405780.
83. O. Yaffe, Y. Guo, L. Z. Tan, D. A. Egger, T. Hull, C. C. Stoumpos, F. Zheng, T. F. Heinz, L. Kronik, M. G. Kanatzidis, J. S. Owen, A. M. Rappe, M. A. Pimenta and L. E. Brus, *Phys. Rev. Lett.*, 2017, **118**, 136001.
84. F. Bertolotti, D. N. Dirin, M. Ibáñez, F. Krumeich, A. Cervellino, R. Frison, O. Voznyy, E. H. Sargent, M. V. Kovalenko, A. Guagliardi and N. Masciocchi, *Nat. Mater.*, 2016, **15**, 987.
85. D. Niesner, M. Hauck, S. Shrestha, I. Levchuk, G. J. Matt, A. Osvet, M. Batentschuk, C. Brabec, H. B. Weber and T. Fauster, *Proceedings of the National Academy of Sciences*, 2018, **115**, 9509-9514.
86. T. Wang, B. Daiber, J. M. Frost, S. A. Mann, E. C. Garnett, A. Walsh and B. Ehrler, *Energy Environ. Sci.*, 2017, **10**, 509-515.
87. F. Zheng, L. Z. Tan, S. Liu and A. M. Rappe, *Nano Lett.*, 2015, **15**, 7794-7800.
88. E. Mosconi, T. Etienne and F. De Angelis, *J. Phys. Chem. Lett.*, 2017, **8**, 2247-2252.
89. M. A. Becker, R. Vaxenburg, G. Nedelcu, P. C. Sercel, A. Shabaev, M. J. Mehl, J. G. Michopoulos, S. G. Lambrakos, N. Bernstein and J. L. Lyons, *Nature*, 2018, **553**, 189.
90. F. Ito, T. Ikoma, K. Akiyama, A. Watanabe and S. Tero-Kubota, *The Journal of Physical Chemistry B*, 2005, **109**, 8707-8717.

91. T. Basel, D. Sun, S. Baniya, R. McLaughlin, H. Choi, O. Kwon and Z. V. Vardeny, *Advanced Electronic Materials*, 2016, **2**.
92. J. Kalinowski, J. Szmytkowski and W. Stampor, *Chem. Phys. Lett.*, 2003, **378**, 380-387.
93. I. V. Tolstov, A. V. Belov, M. G. Kaplunov, I. K. Yakuschenko, N. G. Spitsina, M. M. Triebel and E. L. Frankevich, *J. Lumin.*, 2005, **112**, 368-371.
94. J. Kalinowski, M. Cocchi, D. Virgili, P. Di Marco and V. Fattori, *Chem. Phys. Lett.*, 2003, **380**, 710-715.
95. S. P. Kersten, A. J. Schellekens, B. Koopmans and P. A. Bobbert, *Phys. Rev. Lett.*, 2011, **106**, 197402.
96. J. Kalinowski, M. Cocchi, D. Virgili, V. Fattori and P. Di Marco, *Phys. Rev. B*, 2004, **70**, 205303.
97. B. Hu and Y. Wu, *Nat. Mater.*, 2007, **6**, 985-991.
98. L. He, M. Li, A. Urbas and B. Hu, *Adv. Mater.*, 2014, **26**, 3956-3961.
99. F. Wang, Y. Han, C. S. Lim, Y. Lu, J. Wang, J. Xu, H. Chen, C. Zhang, M. Hong and X. Liu, *Nature*, 2010, **463**, 1061-1065.
100. A. Weller, H. Staerk and R. Treichel, *Faraday Discussions of the Chemical Society*, 1984, **78**, 271-278.
101. D. Rina, F. Yoshihisa, Z. Baowen and T. Yoshifumi, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 1573-1580.
102. H. Zang, Z. Xu and B. Hu, *The Journal of Physical Chemistry B*, 2010, **114**, 5704-5709.
103. M. Li, L. He, H. Xu, M. Shao, J. Tisdale and B. Hu, *J. Phys. Chem. Lett.*, 2015, **6**, 4319-4325.
104. M. Li, H. Wang, L. He, H. Zang, H. Xu and B. Hu, *Appl. Phys. Lett.*, 2014, **105**, 023302.
105. M. Pollnau, D. R. Gamelin, S. R. Lüthi, H. U. Güdel and M. P. Hehlen, *Phys. Rev. B*, 2000, **61**, 3337-3346.
106. Y. Lei, H. Song, L. Yang, L. Yu, Z. Liu, G. Pan, X. Bai and L. Fan, *The Journal of Chemical Physics*, 2005, **123**, 174710.

107. L. van Pieterson, M. F. Reid and A. Meijerink, *Phys. Rev. Lett.*, 2002, **88**, 067405.
108. F. Wang and X. Liu, *Chem. Soc. Rev.*, 2009, **38**, 976-989.
109. S. Heer, K. Kömpe, H. U. Güdel and M. Haase, *Adv. Mater.*, 2004, **16**, 2102-2105.
110. J. Silver, M. I. Martinez-Rubio, T. G. Ireland, G. R. Fern and R. Withnall, *The Journal of Physical Chemistry B*, 2001, **105**, 948-953.
111. Q. Huang, J. Yu, E. Ma and K. Lin, *The Journal of Physical Chemistry C*, 2010, **114**, 4719-4724.
112. H. Staerk, W. Kühnle, R. Treichel and A. Weller, *Chem. Phys. Lett.*, 1985, **118**, 19-24.
113. Q. Bao and K. P. Loh, *ACS Nano*, 2012, **6**, 3677-3694.
114. C.-H. Liu, Y.-C. Chang, T. B. Norris and Z. Zhong, *Nat. Nanotechnol.*, 2014, **9**, 273.
115. M. He, X. Pang, X. Liu, B. Jiang, Y. He, H. Snaith and Z. Lin, *Angew. Chem. Int. Ed.*, 2016, **55**, 4280-4284.
116. M. He, B. Li, X. Cui, B. Jiang, Y. He, Y. Chen, D. O'Neil, P. Szymanski, M. A. El-Sayed, J. Huang and Z. Lin, *Nature Communications*, 2017, **8**, 16045.
117. P. Gambardella, S. Rusponi, M. Veronese, S. S. Dhesi, C. Grazioli, A. Dallmeyer, I. Cabria, R. Zeller, P. H. Dederichs, K. Kern, C. Carbone and H. Brune, *Science*, 2003, **300**, 1130-1133.
118. A.-H. Lu, E. L. Salabas and F. Schüth, *Angew. Chem. Int. Ed.*, 2007, **46**, 1222-1244.
119. C. Pascal, J. L. Pascal, F. Favier, M. L. Elidrissi Moubtassim and C. Payen, *Chem. Mater.*, 1999, **11**, 141-147.
120. T. Hyeon, S. S. Lee, J. Park, Y. Chung and H. B. Na, *J. Am. Chem. Soc.*, 2001, **123**, 12798-12801.
121. S. Sun and H. Zeng, *J. Am. Chem. Soc.*, 2002, **124**, 8204-8205.
122. K. N. Kudin, B. Ozbas, H. C. Schniepp, R. K. Prud'homme, I. A. Aksay and R. Car, *Nano Lett.*, 2008, **8**, 36-41.
123. N. E. Geacintov, F. Van Nostrand, J. F. Becker and J. B. Tinkel, *Biochimica et Biophysica Acta (BBA) - Bioenergetics*, 1972, **267**, 65-79.

124. R. R. Nair, M. Sepioni, I. L. Tsai, O. Lehtinen, J. Keinonen, A. V. Krasheninnikov, T. Thomson, A. K. Geim and I. V. Grigorieva, *Nat Phys*, 2012, **8**, 199-202.
125. H. González-Herrero, J. M. Gómez-Rodríguez, P. Mallet, M. Moaied, J. J. Palacios, C. Salgado, M. M. Ugeda, J.-Y. Veuillen, F. Yndurain and I. Brihuega, *Science*, 2016, **352**, 437-441.
126. A. L. Lin, J. N. B. Rodrigues, C. Su, M. Milletari, K. P. Loh, T. Wu, W. Chen, A. H. C. Neto, S. Adam and A. T. S. Wee, *Sci Rep*, 2015, **5**, 11430.
127. H. Y. Liu, Z. F. Hou, C. H. Hu, Y. Yang and Z. Z. Zhu, *The Journal of Physical Chemistry C*, 2012, **116**, 18193-18201.
128. B. Uchoa, V. N. Kotov, N. Peres and A. C. Neto, *Phys. Rev. Lett.*, 2008, **101**, 026805.
129. F. Lin, X. Tong, Y. Wang, J. Bao and Z. M. Wang, *Nanoscale Res. Lett.*, 2015, **10**, 435.
130. M. Sepioni, R. R. Nair, S. Rablen, J. Narayanan, F. Tuna, R. Winpenny, A. K. Geim and I. V. Grigorieva, *Phys. Rev. Lett.*, 2010, **105**, 207205.
131. K. Parvez, Z.-S. Wu, R. Li, X. Liu, R. Graf, X. Feng and K. Müllen, *J. Am. Chem. Soc.*, 2014, **136**, 6083-6091.
132. A. K. Geim and I. V. Grigorieva, *Nature*, 2013, **499**, 419-425.
133. Y. Liu, N. O. Weiss, X. Duan, H.-C. Cheng, Y. Huang and X. Duan, *Nature Reviews Materials*, 2016, **1**, 16042.
134. G. Konstantatos, M. Badioli, L. Gaudreau, J. Osmond, M. Bernechea, F. P. G. de Arquer, F. Gatti and F. H. L. Koppens, *Nat Nano*, 2012, **7**, 363-368.
135. S. D. Yu and M. Fonin, *New J. Phys.*, 2010, **12**, 125004.
136. E. Kawabe, H. Yamane, R. Sumii, K. Koizumi, Y. Ouchi, K. Seki and K. Kanai, *Org. Electron.*, 2008, **9**, 783-789.
137. L. Yan, M. Wang, N. Raju, A. Epstein, L.-S. Tan, A. Urbas, L. Y. Chiang and B. Hu, *J. Am. Chem. Soc.*, 2012, **134**, 3549-3554.
138. B. J. Lemaire, P. Davidson, J. Ferré, J. P. Jamet, P. Panine, I. Dozov and J. P. Jolivet, *Phys. Rev. Lett.*, 2002, **88**, 125507.

139. P. T. Yin, S. Shah, M. Chhowalla and K.-B. Lee, *Chem. Rev.*, 2015, **115**, 2483-2531.
140. H. Zhu, K. Miyata, Y. Fu, J. Wang, P. P. Joshi, D. Niesner, K. W. Williams, S. Jin and X.-Y. Zhu, *Science*, 2016, **353**, 1409-1413.
141. M. Karakus, S. A. Jensen, F. D'Angelo, D. Turchinovich, M. Bonn and E. Cánovas, *J. Phys. Chem. Lett.*, 2015, **6**, 4991-4996.
142. R. L. Milot, G. E. Eperon, H. J. Snaith, M. B. Johnston and L. M. Herz, *Adv. Funct. Mater.*, 2015, **25**, 6218-6227.
143. S. De Wolf, J. Holovsky, S.-J. Moon, P. Löper, B. Niesen, M. Ledinsky, F.-J. Haug, J.-H. Yum and C. Ballif, *J. Phys. Chem. Lett.*, 2014, **5**, 1035-1039.
144. P. Löper, M. Stuckelberger, B. Niesen, J. Werner, M. Filipič, S.-J. Moon, J.-H. Yum, M. Topič, S. De Wolf and C. Ballif, *J. Phys. Chem. Lett.*, 2015, **6**, 66-71.
145. Y. Yang, Y. Yan, M. Yang, S. Choi, K. Zhu, J. M. Luther and M. C. Beard, *Nat. Commun.*, 2015, **6**, 7961.
146. S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza and H. J. Snaith, *Science*, 2013, **342**, 341-344.
147. D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger and K. Katsiev, *Science*, 2015, **347**, 519-522.
148. Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao and J. Huang, *Science*, 2015, **347**, 967-970.
149. A. A. Zhumekenov, M. I. Saidaminov, M. A. Haque, E. Alarousu, S. P. Sarmah, B. Murali, I. Dursun, X.-H. Miao, A. L. Abdelhady, T. Wu, O. F. Mohammed and O. M. Bakr, *ACS Energy Letters*, 2016, **1**, 32-37.
150. P.-Y. Lin, T. Wu, M. Ahmadi, L. Liu, S. Haacke, T.-F. Guo and B. Hu, *Nano Energy*, 2017, **36**, 95-101.
151. M. Li, L. Li, R. Mukherjee, K. Wang, Q. Liu, Q. Zou, H. Xu, J. Tisdale, Z. Gai and I. N. Ivanov, *Adv. Mater.*, 2017, **29**, 1603667.

152. W. Li, S. Yuan, Y. Zhan and B. Ding, *The Journal of Physical Chemistry C*, 2017, **121**, 9537-9542.
153. G. Xing, N. Mathews, S. S. Lim, N. Yantara, X. Liu, D. Sabba, M. Grätzel, S. Mhaisalkar and T. C. Sum, *Nat. Mater.*, 2014, **13**, 476-480.
154. A. Swarnkar, R. Chuliyil, V. K. Ravi, M. Irfanullah, A. Chowdhury and A. Nag, *Angew. Chem. Int. Ed.*, 2015, **54**, 15424-15428.
155. J. Li, L. Xu, T. Wang, J. Song, J. Chen, J. Xue, Y. Dong, B. Cai, Q. Shan, B. Han and H. Zeng, *Adv. Mater.*, 2017, **29**, 1603885.
156. A. Sadhanala, S. Ahmad, B. Zhao, N. Giesbrecht, P. M. Pearce, F. Deschler, R. L. Z. Hoye, K. C. Gödel, T. Bein, P. Docampo, S. E. Dutton, M. F. L. De Volder and R. H. Friend, *Nano Lett.*, 2015, **15**, 6095-6101.
157. L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Lett.*, 2015, **15**, 3692-3696.
158. X. Y. Chin, D. Cortecchia, J. Yin, A. Bruno and C. Soci, *Nat. Commun.*, 2015, **6**, 7383.
159. C. Motta, F. El-Mellouhi and S. Sanvito, *Scientific Reports*, 2015, **5**, 12746.
160. F. Maddalena, X. Y. Chin, D. Cortecchia, A. Bruno and C. Soci, *ACS Appl. Mat. Interfaces*, 2018, **10**, 37316-37325.
161. Y. Cao, N. Wang, H. Tian, J. Guo, Y. Wei, H. Chen, Y. Miao, W. Zou, K. Pan, Y. He, H. Cao, Y. Ke, M. Xu, Y. Wang, M. Yang, K. Du, Z. Fu, D. Kong, D. Dai, Y. Jin, G. Li, H. Li, Q. Peng, J. Wang and W. Huang, *Nature*, 2018, **562**, 249-253.
162. K. Lin, J. Xing, L. N. Quan, F. P. G. de Arquer, X. Gong, J. Lu, L. Xie, W. Zhao, D. Zhang, C. Yan, W. Li, X. Liu, Y. Lu, J. Kirman, E. H. Sargent, Q. Xiong and Z. Wei, *Nature*, 2018, **562**, 245-248.
163. L. N. Quan, Y. Zhao, F. P. García de Arquer, R. Sabatini, G. Walters, O. Voznyy, R. Comin, Y. Li, J. Z. Fan and H. Tan, *Nano Lett.*, 2017, **17**, 3701-3709.
164. X. Yang, X. Zhang, J. Deng, Z. Chu, Q. Jiang, J. Meng, P. Wang, L. Zhang, Z. Yin and J. You, *Nature Communications*, 2018, **9**, 570.

165. J. Song, J. Li, X. Li, L. Xu, Y. Dong and H. Zeng, *Adv. Mater.*, 2015, **27**, 7162-7167.
166. Y.-H. Kim, C. Wolf, Y.-T. Kim, H. Cho, W. Kwon, S. Do, A. Sadhanala, C. G. Park, S.-W. Rhee, S. H. Im, R. H. Friend and T.-W. Lee, *ACS Nano*, 2017, **11**, 6586-6593.
167. Y.-H. Kim, G.-H. Lee, Y.-T. Kim, C. Wolf, H. J. Yun, W. Kwon, C. G. Park and T.-W. Lee, *Nano Energy*, 2017, **38**, 51-58.
168. J. Im, C. C. Stoumpos, H. Jin, A. J. Freeman and M. G. Kanatzidis, *J. Phys. Chem. Lett.*, 2015, **6**, 3503-3509.
169. C. Katan, L. Pedesseau, M. Kepenekian, A. Rolland and J. Even, *Journal of Materials Chemistry A*, 2015, **3**, 9232-9240.
170. J. Even, L. Pedesseau, J.-M. Jancu and C. Katan, *J. Phys. Chem. Lett.*, 2013, **4**, 2999-3005.
171. Y.-Q. Liu, H.-L. Cui and D. Wei, *The Journal of Physical Chemistry C*, 2018, **122**, 4150-4155.
172. W. Rehman, D. P. McMeekin, J. B. Patel, R. L. Milot, M. B. Johnston, H. J. Snaith and L. M. Herz, *Energy Environ. Sci.*, 2017, **10**, 361-369.
173. D. P. McMeekin, Z. Wang, W. Rehman, F. Pulvirenti, J. B. Patel, N. K. Noel, M. B. Johnston, S. R. Marder, L. M. Herz and H. J. Snaith, *Adv. Mater.*, 2017, **29**, 1607039.
174. D. Bi, W. Tress, M. I. Dar, P. Gao, J. Luo, C. Renevier, K. Schenk, A. Abate, F. Giordano, J.-P. Correa Baena, J.-D. Decoppet, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Grätzel and A. Hagfeldt, *Science Advances*, 2016, **2**, e1501170.
175. J. Lu, L. Jiang, W. Li, F. Li, N. K. Pai, A. D. Scully, C.-M. Tsai, U. Bach, A. N. Simonov, Y.-B. Cheng and L. Spiccia, *Adv. Energy Mater.*, 2017, **7**, 1700444.
176. T. Singh and T. Miyasaka, *Adv. Energy Mater.*, 2018, **8**, 1700677.
177. N. De Marco, H. Zhou, Q. Chen, P. Sun, Z. Liu, L. Meng, E.-P. Yao, Y. Liu, A. Schiffer and Y. Yang, *Nano Lett.*, 2016, **16**, 1009-1016.
178. G. Giorgi, J.-I. Fujisawa, H. Segawa and K. Yamashita, *The Journal of Physical Chemistry C*, 2015, **119**, 4694-4701.

179. J. Zhang, T. Wu, J. Duan, M. Ahmadi, F. Jiang, Y. Zhou and B. Hu, *Nano Energy*, 2017, **38**, 297-303.
180. A. D. Jodlowski, C. Roldán-Carmona, G. Grancini, M. Salado, M. Ralaiarisoa, S. Ahmad, N. Koch, L. Camacho, G. de Miguel and M. K. Nazeeruddin, *Nature Energy*, 2017, **2**, 972-979.
181. J. P. H. Rivett, L. Z. Tan, M. B. Price, S. A. Bourelle, N. J. L. K. Davis, J. Xiao, Y. Zou, R. Middleton, B. Sun, A. M. Rappe, D. Credgington and F. Deschler, *Nature Communications*, 2018, **9**, 3531.
182. Y. Zhai, C. X. Sheng, C. Zhang and Z. V. Vardeny, *Adv. Funct. Mater.*, 2016, **26**, 1617-1627.
183. C. Sheng, C. Zhang, Y. Zhai, K. Mielczarek, W. Wang, W. Ma, A. Zakhidov and Z. V. Vardeny, *Phys. Rev. Lett.*, 2015, **114**, 116601.
184. S. Ma, H. Xu, M. Wang, J. Qin, T. Wu, P. Chen and B. Hu, *Nano Energy*, 2019, **65**, 104004.
185. T. Wu, L. Collins, J. Zhang, P.-Y. Lin, M. Ahmadi, S. Jesse and B. Hu, *ACS Nano*, 2017, **11**, 11542-11549.
186. A. Perumal, S. Shendre, M. Li, Y. K. E. Tay, V. K. Sharma, S. Chen, Z. Wei, Q. Liu, Y. Gao, P. J. S. Buenconsejo, S. T. Tan, C. L. Gan, Q. Xiong, T. C. Sum and H. V. Demir, *Scientific Reports*, 2016, **6**, 36733.

Vita

Hengxing Xu was born in Beitun, Xinjiang autonomous region, China. He received his B.S. degree in Materials Science and Engineering in 2007 from Beijing Institute of Technology, and M.S. degree in Condensed Matter Physics in 2010 from Beijing University of Aeronautics and Astronautics. In August 2013, he attended the Department of Materials Science and Engineering at University of Tennessee-Knoxville for his Ph. D degree. He has been working on magneto-optical effects in low-dimensional light emitting and magnetic materials. He has also been working on exploring spin and polarization effects in metal halide perovskites toward enhanced optoelectronic properties.