Optical properties and applications of anisotropic low-dimensional nanomaterials

He Yang
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A doctoral dissertation completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Electrical Engineering, at a public examination held at the large seminar hall in Micronova on 6th of April 2018 at 12:00.

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Abstract

This thesis focuses on the optical properties and applications of low-dimensional anisotropic nanomaterials, such as carbon nanotubes (CNTs), nanowires (NWs), black phosphorus (BP). The whole thesis can be divided by three main parts. The first part introduces the fabrication methods of various anisotropic nanomaterials. For instance, as-grown CNTs are synthesized and aligned as an array by a mechanical drawing method. As-grown NWs are aligned by a combing method, and our results show that >95% of the NWs are well aligned. Different from CNTs and NWs, BP has the intrinsic anisotropic optical response due to its anisotropic atomic structure. The mechanical exfoliation method for preparation of few-layer BP is presented, which is also applicable for other two-dimensional layered materials.

The second part introduces the optical characterization methods of the nanomaterials studied in this thesis. Various polarization-dependent microscopes are introduced to characterize their anisotropic properties, such as polarized absorption/transmission spectroscopy, polarized Raman microscopy, polarization-resolved optical microscopy. These microscopes provide useful methods to verify the anisotropic optical response of these nanomaterials.

The third part is the most important one in the thesis, which presents the optical applications of these anisotropic nanomaterials. Firstly, aligned CNTs are used in fiber laser systems to modulate the polarization state of the laser output, which shows excellent performance with the degree of polarization of 89.1% at 1 μm (87.5% at 1.5 μm) for linear polarization modulation. We also demonstrate four-wave mixing based photon-pair generation with CNTs. Secondly, photoluminescence of the combed nanowires is examined to be polarization dependent for multifunctional logic gates. We construct all-optical arithmetic devices with NWs, which provide new means for the realization of all-optical logic gates. Lastly, anisotropic two-dimensional nanomaterials (e.g., BP, ReS₂, ReSe₂) are studied to demonstrate their waveplate performance.

Finally, I summarize the whole contents and give my personal outlook on the study of novel anisotropic nanomaterials to explore their applications in both photonic and optoelectronic fields.
Preface

The work presented in this thesis was carried out in the Photonics Group of the Department of Electronics and Nanoengineering, School of Electrical Engineering, Aalto University, between 2013 and 2017. How time flies! I still remember the first day when I arrived in Finland how everything was unfamiliar and new. But now everything has changed, I have learned a lot and I wish to thank everyone who helped me through the past four years during my PhD life.

Firstly, I want to express my sincere and deepest gratitude to my supervisor, Prof. Zhipei Sun, who gave me the opportunity to learn and grow in such an inspiring and creative group. I am greatly impressed by his intelligence, patience and kindness. What Zhipei taught me is much more than doing research, also involves how to make everything serious. He is always there to give me a hand whenever I meet difficulties both inside and outside of the lab. I am beyond my words in gratitude to him.

Then, I would like to thank Dr. Henri Jussila for his guidance during the last two years. His wide spectrum of knowledge and deep understanding of fundamental problems often inspired me to think differently than I originally did. He always has plenty of novel and brave ideas in mind to share, which makes my research experience so interesting and joyful. Thanks for showing me how to fish in many many cases.

Furthermore, I would like to acknowledge Dr. Ya Chen for her great help at my PhD starting time. As my tutor, she guided me patiently in the cleanroom at Micronova. And in the life, she also helped me to solve many problems when I just moved to Finland. I want to thank Dr. Ali Shah and Dr. Elken Abudulai for the great discussion during the time when we shared the same office. Ali showed me a lot on the work of microfabrication, and Elken presented me many interesting things both in Finland and China.

In addition, I am also in dept to thank the collaborators (especially Prof. Qingwen Li from Suzhou Institute of Nano-tech and Nano-bionics in China supplied me the aligned carbon nanotubes, Dr. Guojun Ye and Prof. Xianhui Chen from University of Science and Technology of China supplied black phosphorus samples, Dr. Niko Granqvist supplied the surface plamon resonance sensors) and my colleagues who have always provided the help when I needed to make everything work fine, especially Dr. Hannu-Pekka Komsa, Dr. Ying Tian, Dr. Hua Jiang, Dr. Bo Fu, Anton Autere, Joona-Pekko Kakko, Dr. Sami Kujala, Dr. Marco Mattila, Dr. Ville Pale, Dr. Mikko Ruoho, John Rönn, Dr. Veer Dhaka, Dr. Nan Wei, Hui Xue, Joonas Holmi, Dr. Baitao Zhang, Prof. Maoshuai He, Prof. Jingliang He, Prof. Harri Lipsanen, Prof. Ilkka Tittonen, Prof. Esko I. Kauppinen. You have helped me a lot with research activities, including experimental operations, data analysis and simulations, suggestions and ideas. I have learned a lot from all of you!
At the same time, I want to thank my good friends to share the happiness with me in life at Finland, Zhengjun Liu, Feng Chang, Yadong Wang, Libin Wang, Yunyun Dai, Yongping Liao, Ying Liu, Yameng Bao. Thank you all and wish to enjoy more with you!

The fundings from China Scholarship Council, Nokia Foundation, School of Electrical Engineering, Research Foundation of Helsinki University of Technology are acknowledged for funding my work. Aalto Nanofabrication center at Micronova is specially acknowledged for supporting and maintaining the research infrastructure.

Finally, I want to express my deepest gratitude to my parents and my wife for your unconditional trust and encouragement. None of this work have been possible without your support. Sincerely thank all of you!

Espoo, March 8, 2018,

He Yang
## Contents

- **Preface**
- **Contents**
- **List of Publications**
- **Author’s Contribution**

### 1. Introduction

### 2. Background

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>One-dimensional nanomaterials</td>
<td>5</td>
</tr>
<tr>
<td>2.1.1</td>
<td>Carbon nanotubes (CNTs)</td>
<td>5</td>
</tr>
<tr>
<td>2.1.2</td>
<td>Nanowires</td>
<td>7</td>
</tr>
<tr>
<td>2.2</td>
<td>Two-dimensional (2D) layered materials</td>
<td>8</td>
</tr>
<tr>
<td>2.2.1</td>
<td>Graphene</td>
<td>8</td>
</tr>
<tr>
<td>2.2.2</td>
<td>Black phosphorus (BP)</td>
<td>10</td>
</tr>
<tr>
<td>2.2.3</td>
<td>ReS$_2$ and ReSe$_2$</td>
<td>10</td>
</tr>
</tbody>
</table>

### 3. Fabrication Methods

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>CNTs</td>
<td>13</td>
</tr>
<tr>
<td>3.1.1</td>
<td>Chemical vapor deposition synthesis</td>
<td>13</td>
</tr>
<tr>
<td>3.1.2</td>
<td>CNT alignment</td>
<td>16</td>
</tr>
<tr>
<td>3.2</td>
<td>Nanowires</td>
<td>17</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Metal organic vapor phase epitaxy synthesis</td>
<td>17</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Nanocombing</td>
<td>17</td>
</tr>
<tr>
<td>3.3</td>
<td>2D layered materials</td>
<td>18</td>
</tr>
</tbody>
</table>

### 4. Optical Characterization Methods

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Absorption/Transmittance spectroscopy</td>
<td>23</td>
</tr>
<tr>
<td>4.2</td>
<td>Polarized Raman microscopy</td>
<td>23</td>
</tr>
</tbody>
</table>
This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.


VI H. Jussila, T. A-Owen, H. Yang, G. Hu, S. Aksimsek, N. Graqvist,

Publication I: “Broadband laser polarization control with aligned carbon nanotubes”

The author did the scanning electron microscopy characterization, characterized the polarized Raman and Transmission properties of the aligned carbon nanotubes, measured the polarization controlled laser output results, analysed the results and wrote the manuscript together with the co-authors.

Publication II: “Optical waveplates based on birefringence of anisotropic two-dimensional layered materials”

The author prepared and characterized the samples, conducted the experiments, analysed the results, and wrote the manuscript together with the co-authors.

Publication III: “Multifunctional all-optical logic gates with nanowire networks”

The author did the alignment of the as-grown nanowire samples, performed the optical experiments and wrote the manuscript together with the co-authors.
Publication IV: “Surface plasmon resonance for characterization of large-area atomic-layer graphene film”

The author transferred the graphene film, did the Raman characterization of the graphene film, and wrote the corresponding parts of the manuscript.

Publication V: “Photon-pair generation with a 100 nm thick carbon nanotube film”

The author participated in characterizing the carbon nanotube sample, analyzing the results and writing the corresponding parts of the manuscript.

Publication VI: “New approach for thickness determination of solution-deposited graphene thin films”

The author performed the surface plasmon resonance measurements and wrote the corresponding parts of the manuscript.

Publication VII: “Fe-Ti-O based catalyst for large-chiral-angle single-walled carbon nanotube growth”

The author participated in preparation and growth of carbon nanotubes sample, wrote the corresponding parts of the manuscript.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>One-dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>AC</td>
<td>Armchair</td>
</tr>
<tr>
<td>ACNT</td>
<td>Aligned Carbon Nanotube</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>AL</td>
<td>Atomic layer</td>
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<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>AlGaAs</td>
<td>Aluminum gallium arsenide</td>
</tr>
<tr>
<td>APD</td>
<td>Avalanche photodiode</td>
</tr>
<tr>
<td>AR</td>
<td>Anti-reflection</td>
</tr>
<tr>
<td>BP</td>
<td>Black phosphorus</td>
</tr>
<tr>
<td>CAR</td>
<td>Coincidence to accidental ratio</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction band</td>
</tr>
<tr>
<td>Cc</td>
<td>Coincidence counts</td>
</tr>
<tr>
<td>CW</td>
<td>Continuous wave</td>
</tr>
<tr>
<td>DOP</td>
<td>Degree of polarization</td>
</tr>
<tr>
<td>EDFA</td>
<td>Erbium doped fiber amplifier</td>
</tr>
<tr>
<td>EDFL</td>
<td>Erbium doped fiber laser</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray</td>
</tr>
<tr>
<td>ER</td>
<td>Extinction ratio</td>
</tr>
<tr>
<td>FBG</td>
<td>Fiber Bragg grating</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>FWM</td>
<td>Four-wave mixing</td>
</tr>
<tr>
<td>GaTe</td>
<td>Gallium tellurium</td>
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<tr>
<td>GeS</td>
<td>Germanium sulfide</td>
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<tr>
<td>GSA</td>
<td>Graphene-based saturable absorber</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>-------------</td>
</tr>
<tr>
<td>h-BN</td>
<td>Hexagonal boron nitride</td>
</tr>
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<td>HR</td>
<td>High-reflection</td>
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<td>HRSTEM</td>
<td>High-resolution scanning transmission electronic microscopy</td>
</tr>
<tr>
<td>HWP</td>
<td>Half-wave plate</td>
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<tr>
<td>InP</td>
<td>Indium phosphide</td>
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<tr>
<td>LD</td>
<td>Laser diode</td>
</tr>
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<td>MOVPE</td>
<td>Metal organic vapor phase epitaxy</td>
</tr>
<tr>
<td>NW</td>
<td>Nanowire</td>
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<tr>
<td>OC</td>
<td>Output coupler</td>
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<tr>
<td>PBS</td>
<td>Polarization beam splitter</td>
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<td>PDMS</td>
<td>Polydimetyylisiloksaani</td>
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<tr>
<td>PECVD</td>
<td>Plasmon enhanced chemical vapor deposition</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
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<td>PROM</td>
<td>Polarization-resolved optical microscopy</td>
</tr>
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<td>PRRM</td>
<td>Polarization-resolved Raman microscopy</td>
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<tr>
<td>PTEE</td>
<td>Polytetrafluoroethylene</td>
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<tr>
<td>Q1D</td>
<td>Quasi one-dimensional</td>
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<td>QWP</td>
<td>Quarter-wave plate</td>
</tr>
<tr>
<td>ReS$_2$</td>
<td>Rhenium disulfide</td>
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<tr>
<td>ReSe$_2$</td>
<td>Rhenium diselenide</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SnS</td>
<td>Tin sulfide</td>
</tr>
<tr>
<td>SnSe</td>
<td>Tin selenide</td>
</tr>
<tr>
<td>SPR</td>
<td>Surface plasmon resonance</td>
</tr>
<tr>
<td>SWNT</td>
<td>Single-wall Carbon Nanotube</td>
</tr>
<tr>
<td>THz</td>
<td>Terahertz</td>
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<tr>
<td>Ti</td>
<td>Titanium</td>
</tr>
<tr>
<td>TIR</td>
<td>Total inner reflection</td>
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<tr>
<td>TMD</td>
<td>Transitional metal dichalcogenide</td>
</tr>
<tr>
<td>VB</td>
<td>Valence band</td>
</tr>
<tr>
<td>VLS</td>
<td>Vapor-liquid-solid</td>
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<tr>
<td>WDM</td>
<td>Wavelength division multiplexer</td>
</tr>
<tr>
<td>YDFL</td>
<td>Ytterbium doped fiber laser</td>
</tr>
<tr>
<td>ZZ</td>
<td>Zigzag</td>
</tr>
</tbody>
</table>
List of Symbols

$A_i$  Excitation light wavelength
$B_i$  Polarization direction
$c$  Speed of light
$c_{ij}$  Output of the logic gate
$dB$  Decibel
$e$  ellipticity
$esu$  Electrostatic unit
$eV$  Electron volt
$g$  Raman gain
$h$  Planck constant
$h$  Dirac constant
$k$  Wave vector
$p$  Plasmon momentum
$P_i$  Idler power
$P_p$  Pump power
$P_s$  Signal power
$q$  Quartz
$\tilde{R}$  Raman tensor

$\alpha$  Fine structure constant
$\gamma$  Parametric nonlinearity
$\Delta n$  Birefringence
$\delta$  Phase change
List of Symbols

$\epsilon$  Permittivity

$\theta$  Incident light angle

$\lambda$  Wavelength

$\mu m$  Micron

$\phi$  Input polarization direction

$\varphi$  Rotation angle of the polarization analyzer

$\omega$  Frequency of the incident light
1. Introduction

Since the discovery of birefringence in uniaxial calcite crystals [1], the anisotropic optical response of various materials has been extensively studied and explored for centuries. The intrinsic anisotropy enables the deep understanding of the material properties as well as their applications in various fields. One important application is the polarization optics, such as polarizing beam splitters (PBS) with high extinction ratio (ER), and wave plates. Besides calcite, many other materials with anisotropic crystal structures are explored and studied. For example, Grischkowsky et al. experimentally measured the refractive indices of quartz and sapphire for ordinary and extraordinary rays, which showed birefringence [2]. Masson et al. demonstrated a Terahertz (THz) quarter-wave plate using six pieces of quartz plates [3]. Because of the orientation order, liquid crystals show strong birefringence. And their orientation order can be actively controlled by electric or magnetic field [4, 5]. Some artificial materials (i.e., metamaterials with low symmetry) also show anisotropic responses, which have been used for polarization control [6]. Interestingly, even wood has birefringence due to the fiber orientation [7].

In addition to intrinsic anisotropy of crystal structures, orientated assemblies of nanomaterials with elongated geometrical structures also exhibit anisotropic optical responses. Ren et al. demonstrated a THz polarizer using stacked aligned single-wall carbon nanotubes (SWNTs), which showed excellent broadband polarization-control properties [8]. Wang et al. used an InP nanowire to create a polarization-sensitive nanoscale photodetector [9]. Weller et al. firstly observed the birefringence from highly aligned CdSe nanorods, which attributed to the smectic ordering of nanorod layers [10]. Gacoin et al. assembled parallelly oriented LaPO$_4$ nanorods via blade coating, and the resulting nanorod based films exhibited large birefringence, which was promising for thin-film wave plate ap-
Nowadays, with the development of integrated devices, traditional anisotropic bulk materials are challenging to be integrated into various nanosystems to realize the polarization control. Thus, these abovementioned low-dimensional nanomaterials with various anisotropic optical properties are highly suitable and required in the polarization-dependent (or direction-related) nano-devices. Until now, there have been many nanomaterials showing anisotropic properties. For example, one dimensional (1D) nanorods, nanotubes and nanowires (NWs) were reported for their anisotropic optical characterizations (e.g., Raman, absorption, reflection). Two-dimensional (2D) nanoplates, sheets, and nanoribbons were also studied on their anisotropic, thermal and optical responses. However, most of the works was focused on the fabrication and characterization of these anisotropic nanomaterials, and their promising optical applications were rarely presented. In this thesis, we demonstrate various optical applications (e.g., nanometer-scale polarization controller, polarization induced optical nanoproce...
is used for the generation of photon-pairs. Chapter 6 demonstrates the polarization dependent photoluminescence (PL) property of 1D semiconducting NWs (InP and AlGaAs) for various all-optical logic gates and arithmetic calculators. Chapter 7 introduces the applications of 2D anisotropic materials (BP, ReS$_2$ and ReSe$_2$) based waveplates such as atomically thin optical wave plates. In the last chapter, the summary of the thesis results and the outlook on anisotropic nanomaterials are presented.
2. Background

During the last decades, low dimensional nanomaterials (e.g., CNTs, nanorods and NWs, graphene [12] and transitional metal dichalcogenides (TMDs) [13]) have attracted intensive attraction due to their unique electrical and optical properties. Owing to their unique properties, they have been widely used into various integrated systems (e.g., field-effect transistors [13–16], solar cells [13, 17–19], modulators [20], light-emitting diodes [21–23], ultrafast lasers [24–26]). Among various demonstrated properties (such as high mobility [14, 27], direct-bandgap at monolayer [28], high strength [29]), anisotropic property is very interesting for the applications in various polarization-dependent integrated nano-devices. In this chapter, I will introduce background of the anisotropic low-dimensional nanomaterials reported in my publications.

2.1 One-dimensional nanomaterials

2.1.1 Carbon nanotubes (CNTs)

CNTs are a class of carbon allotropes with a cylindrical nanostructure, which are formed by rolling up graphene layers. SWNTs consist of only one layer of graphene sheet, but multi-wall carbon nanotubes (MWNTs) are formed by several graphene layers. There are many ways to fabricate SWNTs, which affect their diameters and structures. The way the graphene sheet is wrapped is expressed by a pair of indices \((n,m)\), which is defined by the chiral vector \(C_h\):

\[
C_h = m\vec{a}_1 + n\vec{a}_2
\]  

where \(\vec{a}_1\) and \(\vec{a}_2\) are lattice vectors of graphene sheet. As shown in Figure 2.1, \(|\vec{a}_1| = |\vec{a}_2| = a = \sqrt{3}a_{cc}\), where \(a_{cc} = 1.42\ \text{Å}\), expressing the distance...
between neighbouring atoms. The translation vector $\vec{T}$ is normal to the chiral vector $\vec{C}_h$ and parallel to the nanotube axis. The angle $\theta$ between $\vec{C}_h$ and $\vec{a}_1$ is called the chiral angle. Based on the determination of chirality, SWNTs can be divided into three categories: zigzag ($m = 0$ or $\theta = 0^\circ$), armchair ($m = n$ or $\theta = 30^\circ$) and chiral nanotubes (the rest). Based on the determination of chirality, the diameter of SWNTs is expressed as $d = |\vec{C}_h| = a\sqrt{n^2 + m^2 + nm}$ [30]. The chirality of CNTs will determine their optical and electrical properties, even for the CNTs with the same diameter.

Figure 2.1. The unrolled honeycomb lattice of a nanotube [30]. The $\vec{OA}$ and $\vec{OB}$ define the chiral vector $\vec{C}_h$ and the transition vector $\vec{T}$ of the nanotube, respectively.

Because of the high aspect ratio (length/diameter) of the fundamental structure, SWNTs are regarded as naturally anisotropic materials, as illustrated in Figure 2.2 (a). The high structural anisotropy of SWNTs results in the quasi-one-dimensional (Q1D) electronic structure, which leads to a divergent behaviour in the density of states, i.e. van Hove singularity and the enhancement of exciton effects [31, 32]. For such 1D structure, the optical anisotropy in absorption [33, 34] and Raman-scattering spectra [35–37] has been verified to be polarization dependent, which enables polarization-dependent optical devices. However, due to the random orientation of as-grown CNTs (shown in Figure 2.2 (b)), it is difficult to use the CNTs as an anisotropic medium to control the light polarization. So it is necessary to use an isolated CNT or aligned CNTs for both scientific studies and practical applications of the unique anisotropic properties of CNTs. For a group of CNTs, the anisotropic nature of individual CNT is best preserved and explicitly conceived when all CNTs are aligned in the
same direction as an array, as shown in Figure 2.2 (c).

![Image of SWNTs](image)

**Figure 2.2.** (a) Conceptual diagram of SWNTs, showing the typical dimensions of length and diameter [38]. (b) The scanning electron microscopy (SEM) image of an as-grown CNT film and (c) an ACNT film. [Figures (b) and (c) are adopted from Publication I]

To obtain the ACNT array, various alignment techniques have been developed [39]. Based on the growth mechanisms, these techniques are categorized into two groups pertaining to when the alignment is achieved: (a) *in situ* techniques (e.g., plasma-enhanced chemical vapour deposition (PECVD) assisted by catalytic nanoparticles [40, 41], discharge method [42], laser ablation method [43], and thermal chemical vapor deposition (TCVD) method [44]) where alignment is achieved during the CNT growth process and (b) *ex situ* techniques (e.g., aligned by electric fields [45], magnetic fields [46], force fields [47], and other methods [48]) after CNTs are grown. Compared with the *in situ* techniques, the *ex situ* techniques are free of collateral growth restrictions, such as special substrate material and critical growth temperature. A special mechanical pulling method is selected for the preparation of our ACNT optical device, which will be described in Chapter 3. Compared with randomly orientated CNTs based devices, the performance of ACNT-based devices has been improved greatly. For example, the typical strain in ACNT films has been improved by up to an order of magnitude after alignment [49], and thin film transistors based on aligned SWNTs show mobilities up to 40 times higher than randomly orientated devices [50, 51].

### 2.1.2 Nanowires

Similar to CNTs, semiconducting NWs are another 1D nanomaterials with high surface-to-volume ratio. Due to the similar shape, their electrons and holes are strongly confined for various applications, such as polarization-dependent optical and electrical devices [9, 52]. In the past
Background

In the past decade, 1D NWs have been extensively studied on their anisotropic physical responses, such as polarization dependent photodetection [9], polarized PL [52], anisotropic carrier mobility [53]. Due to their subwavelength diameters and strong waveguiding effects [54–56], 1D NWs also have been used to construct all-optical logic components to realize the all-optical nanoprocessors, which are promising to break the limitations of modern integrated circuits. In my Publication III, all-optical nanoproces- sors based on the NWs’ anisotropic property are demonstrated. For the construction of the nanocomputer, nanocombing of NWs is an important fabrication process of our work (Figure 2.3), which is also the basic of the construction of various current NW devices. Many techniques have been developed to align the randomly located as-grown NWs, such as electron beam lithography [57], focused ion beam milling [58], and micromanipulation [59]. The maximum alignment degree reaches as high as 98.5% (±1°) [60]. But these processes are complex and time-consuming. Therefore, in our process, we develop a simple but useful nanocombing method to comb two types of NWs (InP and AlGaAs) at two orthogonal directions, forming crossbar junctions with the alignment degree of ∼ 95% (±10°), which is convenient and useful for the fabrication of NW integrated optoelectronic devices. The detailed process will be introduced in Chapter 3 Fabrication Method.

Figure 2.3. The typical SEM images of the as-grown NWs (a) and combed NWs (b) on a Si substrate. [Publications III]

2.2 Two-dimensional (2D) layered materials

2.2.1 Graphene

Graphene is a 2D allotrope of carbon in which the carbon atoms are covalently bonded in hexagonal crystalline lattice [61]. In the lattice, each carbon atom is tightly bonded by $sp^2$ hybridization, consisting of the orbitals
of $s, p_x, p_y, p_z$ (out of plane $\pi$ bond) [62]. These bonds lead to a unique band structure in graphene. For example, the valence band (VB) and conduction band (CB) meet at the Dirac point leading to a zero band gap, and the energy-momentum shows linearly dispersion at low energies [63, 64]. Electrons in graphene behave as massless 2D Dirac fermions, with an energy-independent Fermion velocity ($v_F$) of $10^6$ m/s [63]. Due to these properties, the optical conductance of monolayer graphene is frequency (energy) independent, which can be described as $\sigma_0 = e^2/4\hbar$ [28, 65], where $e$ is the electron charge and $\hbar$ is the Dirac constant. Then the optical transmittance ($T$) when a beam of light normally transmits graphene (with conductivity $\sigma$) can be written as [65]

$$T = (1 + \frac{2\pi}{c} \sigma_0)^{-2} \approx 1 - \frac{4\pi}{c} \sigma_0 = 1 - \pi\alpha = 0.977$$

where $c$ is the speed of light, $\alpha$ is the fine-structure constant ($\alpha = e^2/\hbar c = \frac{1}{137}$). The optical absorption of monolayer graphene is $\pi\alpha = 2.3\%$ (shown in Figure 2.4), which is uniform in a broad spectral range (e.g., from the visible to infrared spectral regions) [65, 66]. Note that the graphene absorption can be tuned by gating [20, 67, 68].

Due to the linear dispersion of the Dirac fermions, there will be an electron-hole pair in resonance for any wavelength excitation. Interband excitation by ultrafast optical pulses produces a non-equilibrium carrier population in the VB and CB. Time-resolved experiments [69] show two typical relaxation timescales: a faster one $\sim$ 100 fs, usually associated with carrier-carrier intraband collision and phonon emission, and a slower

![Figure 2.4. Transmittance of graphene with different numbers of layer [65].](image-url)
Background

one at ps timescale, which corresponds to interband recombination and cooling of hot phonons [70, 71]. Thus graphene is promising for ultrafast pulse generation [20, 25, 72–84].

2.2.2 Black phosphorus (BP)

Recently, 2D layered materials [85–89] with anisotropic properties have been extensively studied. Especially, BP is an excellent representative among the anisotropic layered materials due to its strong in-plane anisotropy [85, 90–93], widely tunable direct bandgap [94, 95], and high charge-carrier mobility [96, 97] compared with other 2D materials. BP possesses distinctive anisotropic physical properties stemming from its physical structure [98, 99], as shown in Figure 2.5. This intrinsic anisotropic atomic structure provides opportunities for applications that are impossible with highly in-plane-symmetric materials (e.g., typical TMDs [20, 100], graphene [64], and hexagonal boron nitride (h-BN) [101]). For example, the optical absorption [102], birefringence [89, 102–104], Raman-mode vibrational [103, 105], the carrier mobility [97], thermal conductivity [106] and mechanical property [107] have been studied and verified to be anisotropic in BP. Based on these studies, BP has been applied into various polarization-dependent optical devices, such as photodetectors [108], ultra-fast lasers [109, 110].

![Layered crystal structure of BP, showing the relative positioning of two adjacent puckered sheets with linked phosphorus atoms. Figures (a) and (b) are the side-view and top-view illustrations of the crystal structure of BP showing the zigzag (ZZ) and armchair (AC) axes. [Publication II]](image)

2.2.3 ReS$_2$ and ReSe$_2$

Other anisotropic 2D nanomaterials, including ReS$_2$, ReSe$_2$, GeS, SnS, SnSe, GaTe and InSe [111–117], have been reported. Taking ReS$_2$ and ReSe$_2$ as examples, their in-plane anisotropies arise from the Peierls dis-
tortion of the 1T structure [118]. Because of the low-symmetry lattice, their in-plane optical (e.g., Raman response [119]) and electrical (e.g., conductivity [120]) properties are anisotropic. However, compared with BP based devices, suffering from chemical degradation in ambient conditions, ReS$_2$ and ReSe$_2$ based devices are more stable in the environment, implying their potential for practical applications.
3. Fabrication Methods

This chapter reviews the fabrication methods of different low-dimensional materials based devices studied in this thesis. For example, the as-grown CNTs are aligned by a mechanical pulling method [121, 122], the crossbar NW building blocks are prepared with metalorganic vapor phase epitaxy (MOVPE) followed by the developed nanocombing method, and the 2D layered materials (e.g., BP, ReS$_2$, and ReSe$_2$) are prepared by mechanical exfoliation methods [91, 123].

3.1 CNTs

3.1.1 Chemical vapor deposition synthesis

CNTs have attracted intensive attention for various applications (e.g., photonics [124–136]) as they exhibit extraordinarily optical and electrical properties based on their intrinsic 1D nature [30]. Until now, various synthetic methods for producing CNTs have been reported [137, 138]. Among them, catalyst based chemical vapor deposition (CVD) method is the dominant one because this technique is capable of producing large scale CNTs and controlling the number of their carbon shells [139–142]. Normally, the nanosized iron (Fe) particles are adopted as catalysts that are floated in the reactant furnace or dispersed on the substrate. In our work of Publication VII, CNTs are synthesized using substrate-supported CVD technique with Fe-Ti-O solid solution as catalyst, as shown in Figure 3.1. The FeO$_x$ nanoparticles were prepared by hydrolysis of anhydrous ferric chloride (FeCl$_3$). Briefly, FeCl$_3$ with a mass of 0.807 g was dissolved in 5 mL H$_2$O to form a clear solution. The aqueous solution of FeCl$_3$ was added dropwise into 180 mL boiling H$_2$O under vigorous stirring and refluxed for 2 h to form FeO$_x$ nanoparticles. As-prepared FeO$_x$
nanoparticles were casted onto a Si₃N₄ transmission electron microscopy (TEM) grid (DuraSiN mesh). After that, the grid was deposited with 4 nm Ti. The system pressure was kept at 10⁻⁶ Pa during Ti deposition. The catalyst was finally annealed at 900 °C for 20 h in air to facilitate the formation of Fe-Ti-O solid solution. Using this method, it is useful for the growth of CNTs with relatively large diameter and chiral angle.

Figure 3.2 (a) presents a TEM overview of as-prepared carbon nanotubes grown on Fe-Ti-O catalyst, which confirms that the synthesized nanotubes are single-walled. Nanobeam electron diffraction characterization was performed on a total of 52 randomly isolated SWNTs. The deduced (n, m) indices, chiral angles and diameters of SWNTs are checked, which shows no preference to tubes with metallic or semiconducting indices. 19 of 52 SWNTs were identified to be metallic species, comprising 36% of the total, which is close to the theoretically predicted amount (33%). Most of SWNTs (96%) have diameters in the range of 1.0 -2.4 nm, as also demonstrated in Figure 3.2 (b). Although no high chiral selectivity is observed, (14, 8) tube with a chiral angle of 21.1°, is the most abundant species detected in the product. Besides, SWNTs with diameters near 1.2 and 1.3 nm, including (10, 8), (10, 9), (11, 7) and (11, 8) were also observed more frequently than other tube species, occupying 23% of all the SWNTs. Interestingly, most of the tubes (up to 94%) have a chiral angle larger than 15° and the mean angle is 24° with a standard deviation of 5°. Figure 3.2 (c) compares the percentages of Fe-Ti-O grown SWNTs in different chiral angle ranges with those of SWNTs grown on monometallic Fe catalyst. Clearly, SWNTs with large chiral angles (20°-30°) were more frequently detected in the Fe-Ti-O grown products (82%). However, it is difficult to grow high-density CNT films, and it takes long time compared with the floating catalyst based CVD methods.

Figure 3.1. Schematic illustration of substrate-supported Fe-Ti-O solid solution catalyst for CVD growth of SWNTs. [Publication VII]
Figure 3.2. (a) A TEM overview of as-synthesized carbon nanotubes grown on Fe-Ti-O catalyst at 800 °C using CO as the carbon source. (b) Diameter distribution of metallic and semiconducting SWNTs grown on Fe-Ti-O. (c) The distributions of SWNTs grown from Fe-Ti-O and Fe as a function of chiral angle. [Publication VII]

Figure 3.3. CNT growth setup based on spark discharge-based floating catalyst CVD method using Fe as catalyst. [Publication V]

As demonstrated in Figure 3.3, this is the CNT growth setup using spark discharge-based floating catalyst method [137]. In this technique, CNTs are synthesized by spark discharge-based floating CVD method with Fe as catalyst and carbon monoxide as carbon precursor. The CNT film grown using this method has high purity and quality, and thus does not need any purification process, which simplifies the fabrication and integration process for the SWNT-based photonic applications. In Publication V, we use this method to prepare a CNT film for photon-pair generation. The typical SWNTs and bundle lengths are around several micrometers. The nanotube density is estimated at ~500 nanotubes per square micrometer.
3.1.2 CNT alignment

CNTs have great potential in a wide range of applications such as mechanical memory elements [143], electron field emitters [144–146], quantum resistors [147] and transistors [148]. In particular, the realization of ACNTs has resulted in the demonstration of a variety of unique devices, which performance is dramatically improved compared with their unaligned counterparts. For example, the strain in ACNT films is reduced by an order of magnitude after alignment [49], thin film transistors based on aligned SWNTs show mobilities up to 40 times higher than randomly orientated devices [50, 51]. The better output performance, compared with non-aligned CNT-based devices, implies the importance of CNT alignment. In our work, an ex-situ alignment technique, by mechanically drawing from the spinnable CNT arrays, is adopted to prepare the CNT-based optical polarization devices.

Firstly, the spinnable nanotube arrays were grown on a silicon substrate, which were synthesized in a 5-inch quartz tube at 750 °C by CVD method [121, 122]. After preparing the spinnable nanotube arrays, the ACNT sheet was drawn from the arrays under the help of the rotating spindle. The preparation setup is shown in Figure 3.4 (a). Before the spindle starting, a CNT sheet was firstly drawn from one side of a spinnable array using a blade and then attached on a spindle that was covered by a 40 μm thick polytetrafluoroethylene (PTFE) film. A small angle (5-10°) was kept between the nanotube sheet and the array substrate during the drawing. The winding rate was set at ~1 cm/s. Ethanol was sprayed onto the nanotubes during or after the winding process. When the winding was finished, the obtained ACNT film was put in a drier at 80 °C overnight to remove ethanol. The ACNT film together with the PTEF film was taken off the spindle, followed by carefully peeling off the ACNT film from the PTEF film. For our purpose, the off-peeled ACNT film was directly pressed onto a transparent 1-inch quartz substrate. The prepared ACNT optical device is shown in Figure 3.4 (b). Figure 3.4 (c) is the SEM image of the ACNT film on the quartz substrate, which shows good alignment of CNTs.
3.2 Nanowires

3.2.1 Metal organic vapor phase epitaxy synthesis

In Publication III, the NWs were grown on silicon substrates by using Au-nanoparticle assisted vapor-liquid-solid (VLS) growth method inside a horizontal flow MOVPE reactor [149–152]. Prior to the growth, the substrates were firstly immersed in acetone and isopropanol inside an ultrasonic, followed by 2 minutes rinse in deionized water. 40 nm and 60 nm diameter gold nanoparticles from a colloidal solution were used as catalyst for VLS growth of InP and AlGaAs NWs, respectively. The diameter of the Au particle determines the diameter of the NWs. For the growth of different wires, different sources were selected. For example, for the growth of InP NWs, the In and P sources were simultaneously introduced into the reactor. The length of NWs was determined by the growth time. The longer growth time, the longer NWs length.

3.2.2 Nanocombing

After the synthesis, the as-grown vertical NWs are not practical for applications, as most device structures and fabrication techniques require horizontal geometries. Thus, the nanocombing process to re-orientate the NWs is important to broaden their applications. In our process, the as-grown NWs were transferred onto a glass substrate by using a top-down nanocombing method (i.e., mechanically sliding the NW substrate over the target substrate along one direction). This technique allows the randomly directed NWs on silicon substrates to self-align in the horizontal plane and point towards one direction. Thus, the crossbar NW structures
Fabrication Methods

of InP and AlGaAs NWs were fabricated by combing InP NWs along one direction and AlGaAs NWs along the perpendicular direction. Note that after combing the NWs of the first material (InP), a 100 nm thick SiO\textsubscript{2} layer was deposited (grown by PECVD with the model of Oxford Instruments PECVD 80+) to isolate these NWs from another material (AlGaAs) based NWs. As shown in Figure 3.5, our nanocombing technique enables the realization of multiple crossbar NW junctions on the target substrate.

![Figure 3.5](image.png)

**Figure 3.5.** SEM image of combed NWs. (a) Combed InP NWs, and (b) InP and AlGaAs NWs combed perpendicularly. In (b) InP NWs are combed along the vertical direction and AlGaAs NWs along the horizontal direction. [Publication III]

To estimate the accuracy of the combing, we calculated the combing statistics of NWs by using a custom Matlab program which recognized the SEM image of NWs, from which the NW angle was plotted in histogram (see Figure 3.6). In typical statistics, the NW alignment performance was evaluated over 100 NWs. NWs recognized by our program were marked with different colors. The typical histograms showed that after a single combing step, \(\sim 95\%\) of NWs pointed along the same direction within an alignment error of \(\pm 10^\circ\).

3.3 2D layered materials

With the intensive study on TMD materials, micro-mechanical cleavage method has been widely applied for the preparation of atomically thin layered materials because of their weak interlayer van der Waals force [91, 153]. Here, we take BP as an example to demonstrate the preparation method and transfer process of various 2D materials. The exfoliation mechanics in this method is that the scotch tape is applied to the BP bulk
Fabrication Methods

**Figure 3.6.** NWs combing statistics. (a) The SEM images were used to obtain the NW alignment statistics, with the recognized NWs (95% of the wires) illustrated with different colors. (b) Histograms showed the combing statistics. The solid line showed the fitted Gaussian distribution which indicates that 95% of the NWs pointed along the same direction within an alignment error of ± 10°. [Publication III]

crystal surface and thus exerts normal force. If we repeat this exfoliation process by several more times, the flake layer becomes thinner and thinner. Finally we will get few-atomic-thick flakes, as shown in Figure 3.7 (a).

**Figure 3.7.** (a) Optical image of a piece of mechanically exfoliated BP flake on glass substrate. (b) Schematic diagram of the experimental setup employed for the all-dry transfer process.

After exfoliation, the exfoliated flakes are transferred to the target substrate using the setup shown in Figure 3.7 (b). We take BP flakes as an example to illustrate the detailed dry-transfer process [91, 154]. And the optical images during the transfer process are illustrated in Figure 3.8. A piece of transparent flexible and viscoelastic Polydimetyylisiloksaani (PDMS) film is used as supporting layer during the transfer, which is firstly stamped on a glass substrate [91]. Because both the glass substrate and PDMS film are transparent, either reflection or transmission mode microscopy can be used to find the thin flakes. As the size of the flake is normally limited to several tens of μm, it takes some efforts to find thin flakes under the help of microscopy. After finding the right flake,
the small piece of PDMS film with flakes on the surface is cutted by a
knife, then it is placed onto the transferred stage with the help of a trans-
parent glass holder. The transferred stage is also monitored by another
microscopy, which helps to place the flake at the specified position. Af-
ter slowly and slightly lowering down the glass holder until it is touched
to the target sample, we can peel off the PDMS film from the sample
slowly. Then the flake is transferred to the right position successfully. In
addition to BP, most of other 2D layered materials can be exfoliated and
transferred to the specified position using the same process and setup.
For example, I have fabricated molybdenum idsulfide (MoS$_{2}$) [155] and
transfered it onto SiO$_{2}$/Si substrate for second and third-harmonic optical
frequency generation [155], as shown in Figure 3.9 (a).

After the transfer, thicknesses of various flakes were identified by op-
tical contrast, Raman and PL measurements. For example, as shown in
Figure 3.9 (a), the optical contrast from the MoS$_{2}$ flake differs between
different parts. This suggests variations within the flake thickness.

Three parts (marked with A, B, C) were characterized in more detail,
Raman spectra measured from these locations are shown in Figure 3.9 (b).
Two Raman modes are observed in all spectra close to the wavenumbers
of $\sim 385$ cm$^{-1}$ and $\sim 409$ cm$^{-1}$. These Raman peaks originate from the
in-plane $E_{2g}^{1}$ and out-of-plane $A_{1g}$ vibration modes [156], respectively. It
has been reported that the separation of Raman peaks can provide a good
measurement for the flake thickness [157]. The Raman peak separation
in bulk MoS$_{2}$ is $\sim 26$ cm$^{-1}$. In general, a peak separation of $\sim 19$ cm$^{-1}$ is
considered a value typically measured from monolayer MoS$_{2}$ flakes [157].
In our case, the Raman mode separation is calculated as 18.7 cm$^{-1}$, 18.8
cm$^{-1}$, 21.5 cm$^{-1}$ from the fitted Lorentzian line profiles in the locations
A, B and C, respectively. Therefore, this implies that the flake thickness
in areas A and B is single layer and the area C is bilayer.

In addition to the Raman measurements, PL spectra were measured
from these areas to further verify the flake thickness. In fact, the obser-
vation of strong PL from the exfoliated MoS$_{2}$ flakes also provides informa-
tion about the flake thickness. Figure 3.9 (c) shows that the measured PL
spectra from three different areas marked in Figure 3.9 (a). As expected,
well-resolvable PL is observed from all locations. The PL spectra pos-
sess two transitions at the wavelengths of $\sim 630$ nm and $\sim 680$ nm with
their energy difference equaling the spin-orbit coupling energy [158]. The
decrease in the PL signal intensity from location A to location C (i.e., in-
tensity decreases with increasing flake thickness) is in agreement with the Raman results providing extra proof for the correctness of the layer thickness [158].

![Fabrication Methods](image)

**Figure 3.8.** The images show the whole process of transferring a BP flake to the specified position on a SiO$_2$/Si substrate. (a)-(h) Optical micrograph obtained during the process. (a) A few-layer BP flake is identified on the surface of the viscoelastic PDMS stamp. (b) The selected flake on PDMS is separated by cutting this PDMS area. (c) The few-layer BP flake is aligned on top of the specified position with a three-axis micrometer positioner. (d) Once the flake is aligned, the sample is brought into contact with the substrate. During this process the few-layer BP flake is gradually focused. (e) The flake is half touched into the specified area, which could be easily seen from the touching area of PDMS. (f) The flake is fully touched onto the substrate. (g) After touching, PDMS is slowly peeled off from the substrate, only leaving the flake on the substrate. (h) The optical image shows that the transferred BP flake is placed at the specific position.

![Fabrication Methods](image)

**Figure 3.9.** (a) Optical image of the mechanically exfoliated MoS$_2$ flake. (b) Raman and (c) PL spectra from the areas marked with A-C in (a) [155].
Fabrication Methods
4. Optical Characterization Methods

This chapter reviews the optical characterization methods I used to study the optical properties of various low-dimensional materials in this thesis, such as ACNTs, NWs and 2D materials. For example, the polarized optical characterization methods (e.g., polarized Raman microscopy, polarized transmittance microscopy, polarization-resolved optical microscopy, polarization PL spectroscopy) are discussed in detail.

4.1 Absorption/Transmittance spectroscopy

The transmittance of our ACNT device along two orthogonal directions (i.e., when the polarization direction of the input light is parallel or perpendicular to the CNT alignment direction) is measured by polarized absorption/transmittance spectroscopy (Perkin-Elmer Lambda 950). The measurement wavelength is between 300 nm and 2000 nm. In the Perkin-Elmer Lambda 950 spectrometer the prealigned and prefocused deuterium and tungsten lamps are used as light sources. The light is splitted into two optical paths with a beam splitter, one for reference and another for the sample characterization. During the measurement, a polarizer is inserted into the optical path (before the sample) to obtain the linearly-polarized light beam for the measurement of polarized absorption and transmittance properties.

4.2 Polarized Raman microscopy

Raman microscopy is an important tool typically used for chemical identification, characterization of molecular structures and effects of bonding [159]. It is a light scattering technique, and can be thought of a process where light interacts with the sample to produce scattered radiations.
The scattered light includes not only the light with wavelength identical to the incident light wavelength (Rayleigh scattering), but also a small amount of radiation at different wavelengths (Raman scattering) [160]. If the scattered light has less energy than the incident light, the scattering process is called Stokes Raman scattering. Otherwise, it is called anti-Stokes Raman scattering. Compared to Rayleigh scattering, Raman scattered signal is very weak. Normally, approximately $1 \times 10^{-7}$ of the scattered light is Raman signal [161].

For anisotropic materials, their Raman vibration modes show different intensities along different crystal axis directions. So we can use a polarized Raman microscopy to analysis their asymmetric structure information. The difference between normal Raman microscopy and polarized Raman microscopy is that the excitation laser is linearly-polarized, and a polarization analyser is installed in the beam path between the sample and the spectrometer. In our measurements (as shown in Publication I and II), the excitation laser output at 532 nm wavelength was linearly polarized. A half-wave plate was inserted into the optical path between the laser and the sample to change the polarization direction of the excitation laser. The measured polarization dependent Raman spectra provide useful information on the structural orientation of anisotropic materials, such as birefringent crystals [89], liquid crystals [162].

4.3 Polarization-resolved optical microscopy

Polarization-resolved optical microscopy (PROM) uses polarized light to observe and photograph samples that are visible mainly due to their optically anisotropic characteristics. Publication II demonstrates the PROM images of different anisotropic 2D layered materials. In the structure of a PROM, shown in Figure 4.1, one polarizer is equipped before the sample, and the other polarizer (polarization analyzer) is placed in the optical pathway between the objective rear aperture and the camera port. When a beam of polarized light transmits through a birefringent sample, two individual wave components will be produced, which are polarized in mutually perpendicular planes. The velocities of the two components, typically named the ordinary and extraordinary wavefronts, are different and varied with the propagation direction through the sample. After passing the sample, the light components become out of phase, and are recombined with constructive and destructive interference when they pass through
the analyzer. This is the basic working principle of the PROM. By employing this technique, we can easily distinguish whether the sample is isotropic or anisotropic. In our measurements (details in Publication II), three types of 2D materials (BP, ReS$_2$, and ReSe$_2$) are tested to examine their birefringence.

4.4 Surface plasmon based thickness measurement

Surface plasmon resonance (SPR) describes the resonance of conduction electrons at the interface stimulated by incident light [164], which is capable of measuring many optical properties (i.e., refractive index, thickness, absorption) of nm-level thick film (which is anisotropy in the in-plane and perpendicular directions) when full angular spectra are measured [165]. SPR is similar to ellipsometry in being a non-invasive optical characterization technique, but SPR uses a noble metal coating on sensors (typically gold) to create a highly sensitive evanescent field at the metal surface, thus creating conditions which are extremely sensitive to the small changes in the close vicinity of the surface (∼300 nm). Surface plasmons can be excited by p-polarized light under the resonance condition (shown in Figure 4.2). In order to excite surface plasmon in a resonant manner, a beam of polarized visible light is normally used, which is required to match its momentum (or wave factor) to that of the plasmon. A theo-
tactical description on the resonance condition is obtained by solving the Maxwell equations for a multilayer optical system [165], which provides the following mathematical solution for the resonance condition:

$$\frac{\omega}{c}\sqrt{\varepsilon_0 \sin \theta} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}}$$ (4.1)

where $\omega$ is the frequency of the incident light, $c$ is the speed of light in vacuum, and $\varepsilon_0$, $\varepsilon_1$ and $\varepsilon_2$ are the permittivities of the prism, the adjacent medium and SPR metal layer, respectively. As seen from Eq 4.1, it is insufficient to determine the complex permittivity and the thickness of the samples by only measuring the SPR angle, and another independent information is necessary for unique determination of the complex refractive index of the material. In fact, the attenuated total reflection intensity data (TIR angle) can also be found from the measured SPR curves, which can be used as a second independent variable parameter. In our Publication IV and VI, the complex permittivity and thickness of graphene were obtained simultaneously for a multilayer system. It was conducted by BioNavis LayerSolver software, which fitted the solution of Maxwell equations for a multilayer optical system to the measured reflectance spectrum obtained in a Kretschmann configuration using a transfer matrix formalism of $2 \times 2$ matrices.

**Figure 4.2.** Schematic illustration of the Kretschmann configuration used in our SPR measurements. This configuration clearly shows the SPR measurement process. (a) When the projected wave vector ($k_x$) of the incident light does not match the momentum of surface plasmon ($k_{sp}$), no excitation occurs. (b) At a certain incident light angle ($\theta$), the projected wave vector of the incident light matches the wave vector of the surface plasmons. [Publication IV]

Here we list a graphene film as an example to characterize the optical constants by SPR method. As shown in Figure 4.3, the SPR peaks show strong shifts on both bare $\text{Al}_2\text{O}_3$ and bare Au-coated sensors. For instance, the resonance peak (black curve) of the pure $\text{Al}_2\text{O}_3$ sensor measured using a 670 nm laser for excitation is at 44.58°, while for 1L (blue curve), 2L (cyan curve), and 3L (green curve) graphene samples, they are at 44.93°,
45.19°, and 45.5°, respectively. For a repetition experiment of a different graphene batch on a different sensor, the background was 44.64° and 1L was 44.98°. As expected, the SPR angle difference between the different sensors for both the background and the monolayer graphene is extremely small (i.e., <0.1°), proving the good repeatability of the SPR-based characterization method for large area samples. Furthermore, the SPR peak shift is almost 1°/nm in both cases (assuming that the CVD graphene layer thickness is 0.335 nm). Such large SPR angle shift in graphene is due to the significantly high refractive index in graphene. On the other hand, the resonance peak of the sample with graphene layer on the Au sensor locates at 43.12° and shift slightly less than 0.6°/nm for the same incident wavelength, shown in Figure 4.3 (b). Therefore, the Al₂O₃ sensor gives a better contrast (change of SPR peak) for the deposited graphene layer, which gives the refractive index of graphene of 3.135 at 670 nm. To accurately obtain the graphene refractive index and the layer thickness, the SPR measurements were also performed using a 785 nm light for excitation, shown in Figure 4.3 (c) and (d). The measured results give that the refractive index of graphene is 3.132 at 785 nm.

Further, we also have shown that SPR can be used to accurately measure the thickness of inkjet-printed graphene thin films. Our results demonstrate that the thickness of graphene thin films has a linear correlation with the number of printing repetitions (~ 0.95 nm thickness increase per printing repetition). The thickness obtained by SPR is ~ 1.3 and ~ 1.5 times smaller than that measured using AFM and the stylus profilometer, respectively. We suggest that the apparent difference is due to the different averaging schemes as the SPR method gives less weight to the surface roughness caused by the isolated and protruding graphene flakes in the porous graphene thin film. In addition to the thickness, the SPR method also reveals the complex refractive index of the thin film, which is significantly lower than that measured from the micromechanically exfoliated or CVD-grown graphene samples. This is due to the high porosity of the thin film resulting from decomposition of the PVP polymer stabilizer in the ink formulation. The extinction coefficient and the thickness values of graphene obtained by SPR measurements match the measured absorbance data better than those obtained using AFM and the stylus profilometer. We therefore strongly believe that SPR could be exploited as a fast, cost-effective, and accurate characterization technique for solution processed graphene thin films.
Finally, we conclude that this significantly large SPR shift easily enables the thickness determination of a large area thin film, as shown in Publication IV and VI. Therefore, SPR method can perform fast and cost-effective simultaneous characterization of various parameters (e.g. thickness, optical constants) of thin films at the atomic-scale resolution.

**Figure 4.3.** SPR curves of a graphene film on [(a) and (c)] $\text{Al}_2\text{O}_3$ and [(b) and (d)] Au sensors. The fits (dashed red curves) are performed separately for each measurement. The laser excitation wavelength is 670 nm in (a) and (b) and 785 nm in (c) and (d). [Publication IV]
5. CNTs based linear and nonlinear photonic devices

This chapter reviews the linear and nonlinear photonic applications based on CNTs. Firstly, the linear anisotropic optical properties (e.g., polarized Raman spectrum, polarization absorption) of ACNTs are reviewed. Based on these properties, we integrate the ACNTs into fiber laser systems to control the output polarization. Secondly, we introduce the CNTs based FWM for quantum light sources.

5.1 CNTs based polarizer

Due to their unique structural confinement, ACNTs have been demonstrated in various applications, such as solar cells [166], sensors [167], thermal interface materials [168], infrared and THz sources/detectors [169, 170], and saturable absorbers [171, 172]. It has underscored better performance compared to their randomly orientated counterparts. In particular, ACNTs have strong optical anisotropic characteristics, enabling optical polarizer applications, with superior performance when compared to the conventional bulk polarizers (e.g., prisms and fiber Bragg grating (FBG) [173, 174]), such as easy fabrication, broad operation bandwidth (from ultraviolet [175], visible [176], infrared to THz range [177]), and a high extinction ratio (up to 30 dB [169]).

Laser polarization control plays an important role in a wide range of applications, such as liquid crystal devices, polarization diversity detection in communications and range finding. However, the performance of laser polarization control by ACNTs was not examined. Our work in publication I demonstrates the ACNTs’ anisotropic properties and their polarization control performance in broadband (at 1 and 1.5 \( \mu \)m) laser systems.
5.1.1 Anisotropic optical properties of CNT polarizer

For ACNTs, their Raman scattering intensity varies with different excitation polarization directions. In our experiment, polarized Raman spectra are obtained by changing the input polarization direction ($\phi$) of the excitation laser from 0° to 360° with respect to the CNT alignment direction. When $\phi = 0^\circ$ and $\phi = 90^\circ$, the incident excitation polarization direction is parallel and perpendicular to the ACNT alignment direction, respectively. Typical Raman spectra (Figure 5.1(a)) shows three dominating features, namely D, G, and G' (or 2D) modes, as typically observed for few-wall CNTs [178]. It has been reported that the G-band of Raman modes at around 1580 cm$^{-1}$ is highly sensitive to CNT alignment direction. When we change the angle $\phi$, the intensities of the G-peak and D-peak change from the maximum (at $\phi = 0^\circ$) to the minimum (at $\phi = 90^\circ$), which is in accordance with the polarized absorbance of the ACNTs. The ratio between the maximum and the minimum intensity is $\sim 22$. In our study, the G-peak intensity at different angles $\phi$ is presented in Figure 5.1(b). It indicates that the Raman scattering intensity of ACNTs is sensitive to the polarization direction of the pump light, which is in good agreement with the equation: $I(\phi) \propto \cos^2(\phi)$ for ACNTs. Such anisotropic Raman properties clearly show that CNTs are well aligned.

![Figure 5.1](image)

**Figure 5.1.** (a) Polarized Raman spectra of the ACNT device under the excited laser polarization direction parallel and perpendicular to the CNT alignment direction. (b) G-peak Raman intensity as a function of the angle, and the intensity fitting. [Publication I]

Because of the aligned structure, the optical absorption of the ACNT device along two perpendicular directions is different. As shown in Figure 5.2 (a), the polarized transmittance of the device in the two perpendicular directions (i.e., the polarization direction is parallel and perpendicular to the alignment direction) is different. When the incident light polarization is perpendicular to the ACNT alignment direction, the transmittance is
CNTs based linear and nonlinear photonic devices

\[ \sim 94\% \text{ at } 1.8 \mu m, \text{ which is mainly attributed to the Fresnel loss (} \sim 6\% \text{) of the quartz substrate. While for the parallel polarization light input, the transmittance is } \sim 82\% \text{ at } 1.8 \mu m. \text{ The result identifies the optical anisotropic absorption of our ACNT device. The difference between two orthogonal directions is } \sim 12\% \text{ at } 1.8 \mu m (\sim 16\% \text{ at } 300 \text{ nm, as shown in Figure } 5.2 \text{ (b)), which is comparable to the typical performance reported for ACNTs (from } 15\% \text{ to } 20\% \text{ at different wavelengths [169, 176]).} \]

\[\text{Figure 5.2. (a) Transmittance of the ACNT device with the polarization direction of the incident light parallel and perpendicular to the ACNT aligned direction. (b) The transmittance difference between the two orthogonal directions for the ACNT device. [Publication I]}\]

\[\text{5.1.2 Laser polarization control}\]

To investigate the laser polarization control performance, our ACNT device was firstly inserted into an Erbium-doped fiber laser operated at the laser emission wavelength of 1.5 \mu m. After laser output, one polarization analyzer was placed to examine the output polarization performance.

\[\text{Figure 5.3. Experimental results at } 1.5 \mu m: \text{ (a) normalized output power as a function of polarization analyser angle of our ACNT based laser, and the cosine function fitting of the experimental data. (b) DOP and ER versus pump power, and the inset figure is the normalized output power of the laser with a quartz reference as a function of polarization analyser angle. [Publication I]}\]
After inserting the ACNT device into the laser resonator, we firstly fixed the alignment direction of ACNTs vertical to the horizontal plane in the free space. The output laser power after the polarization analyzer was recorded by changing the angle $\varphi$ from $0^\circ$ to $360^\circ$, where $\varphi$ means the angle between the axis of the polarization analyzer and the vertical direction in free space. The experimental results are illustrated in Figure 5.3 (a), fitted well with the cosine function, i.e., the minimum output power is close to zero at the angle $\varphi$ of $0^\circ$, while the maximum power is located at the angle $\varphi$ of $90^\circ$. It shows that the output polarization of the laser is changed from the random-polarization state to the linear-polarization state, after insertion of our ACNT device into the laser cavity. In order to fully study the performance of intra-cavity polarization control of the ACNT device, the CNT alignment direction was rotated from vertical to horizontal orientation for comparison. The corresponding results are also shown in Figure 5.3 (a). It is observed that the whole curve shifted $90^\circ$ when compared to the one with the vertical placement case of the ACNT device. The result suggests that the laser output with the ACNT device is still linearly-polarized, but the laser output polarization direction rotated with the rotation of the ACNT device. This demonstrates that the polarization state of our laser output can be simply controlled by rotating the intra-cavity ACNT device. Figure 5.3 (b) summarizes the degree of polarization (DOP) and ER of our ACNT based laser versus pump power. The DOP and ER are defined as $DOP = (P_{\text{max}} - P_{\text{min}})/(P_{\text{max}} + P_{\text{min}})$, $ER = P_{\text{max}}/P_{\text{min}}$, where $P_{\text{max}}$ and $P_{\text{min}}$ are the maximum and minimum output power given by the measured results shown in Figure 5.3 (b). The maximum DOP of our ACNT laser is $87.5\%$ at the pump power of $\sim75$ mW, 10 times higher than the DOP of the laser with the quartz reference ($\sim8\%$, as shown in the inset of Figure 5.3 (b)). The corresponding ER of our ACNT laser is $\sim12$ dB, around 8 times higher than the value of the laser with the quartz reference ($\sim1.5$ dB). The ER is $\sim9.8$ dB (with $81\%$ of DOP) at the maximum output power of $1.6$ mW. The DOP and ER performance is pretty unchanged even when the pump power was high ($>100$ mW). This is because the anisotropic absorption of ACNTs dominates the laser output polarization performance.

The ACNT device was also inserted into a $1\,\mu$m laser system with a ytterbium doped gain fiber to examine the broadband modulation performance. The laser system was constructed with the identical structure as the $1.5\,\mu$m laser system except the different gain fibers (see the struc-
ture in Publication I). The laser polarization control results at 1 μm are presented in Figure 5.4 (a), which shows the similar polarization control results that the polarization state can be controlled by our ACNT device. Figure 5.4 (b) summarizes the DOP and ER versus pump power at 1 μm. The DOP reaches ~ 89% at the pump power of 59.4 mW (in contrast to the DOP of 2.9% with the quartz reference in the laser cavity). It decreases slightly as we increase the pump power, which also confirms good polarization dynamics control of our 1 μm fiber laser with the ACNT device. The maximum ER is ~ 12.4 dB, comparable to the result achieved at 1.5 μm.

![Figure 5.4: Experimental results at 1 μm: (a) normalized output power as a function of angle with the polarization analyser, and the cosine function fitting of the experimental data. (b) DOP and ER versus pump power, and the inset figure is the normalized output power of the laser with the quartz reference as a function of polarization analyser angle when the laser is with the quartz reference. [Publication I]](image)

In conclusion, our experimental results successfully show that our ACNT device can be utilized for laser polarization control. The ACNT device shows great potential as a polarization controller in a wide range of photonic applications where linear polarization is required.

### 5.2 CNTs based photon-pair source

FWM is a typical parametric process originating from third-order nonlinear susceptibility (χ(3)), which has useful applications, such as optical switching, amplification and wavelength conversion [179, 180]. It typically occurs when input beams at three different frequencies interact in the medium, producing beams at new wavelengths. Such a nonlinear process requires matching of the frequencies as well as the wave vectors, corresponding to the energy conservation and momentum conservation,
respectively. In particular, when two of the three launched frequencies coincide, the phase matching condition can be satisfied, known as degenerate FWM. The equation for this case can be written: \( \omega_i = 2\omega_p - \omega_s \), where \( \omega_p, \omega_s, \omega_i \) are the frequencies of the pump, signal and idler optical wave. As shown in Figure 5.5, when a weak signal at \( \omega_s \) is launched into a non-linear medium together with the pump at \( \omega_p \), the signal can be amplified accompany with a new wave (\( \omega_i \)) generation.

Figure 5.5. Degenerate FWM process.

Currently, spontaneous FWM plays a dominant role in the generation of high-purity photon pairs at telecom wavelengths based on Kerr effect [181–186]. However, most FWM-based photon-pair sources utilize waveguide structures to enhance the Kerr nonlinearity, such as silica optical fibers [181, 182], silicon-on-insulator waveguides [185, 186]. Due to their large size, it is difficult to integrate them into compact and scalable devices for quantum information applications.

Because of their extraordinary optical and electrical properties, CNTs have been used for various nonlinear all-optical devices (e.g., wavelength converters [187, 188], optical limiters [189], ultrafast pulsed lasers [125–136, 190–196]). Also, it has been reported that the optical quantum devices based on CNTs exhibit single-photon quantum correlation [197–200]. In Publication V, we demonstrated that SWNTs can be used for the photon-pair generation based on FWM.

To measure the conversion efficiency of stimulated FWM in the SWNT film, fabricated by spark discharge-based floating catalyst method (discussed in Chapter 3), a pump-probe configuration was used, as shown in Figure 5.6. The pump beam was from a ultrafast fiber laser at the wavelength of 1550.1 nm, and the probe beam was from another fiber laser at
the idler wavelength of 1555.68 nm. The two beams interacted with the SWNT film, generating a new signal at the wavelength of 1544.56 nm. The signal intensity was measured by an avalanche photodiode (APD1). We plotted the ratio between the signal power ($P_s$) and the idler power ($P_i$) as a function of the pump power ($P_p$) for the SWNT device in Figure 5.7. To remove the effect from the substrate, the same measurement from a reference fused quartz was also performed, as shown in the inset of Figure 5.7. It showed that the conversion efficiency of the SWNT film was about 100-1000 times larger than the reference quartz sample, but the thickness of the SWNT film was $10^4$ times thinner than the reference sample ($\sim$ 1mm). During the measurements, we did not observe any significant change of signal counts at the interface between the SWNT film and the fused quartz substrate. This denotes that nonlinear optical interaction at the interface between the SWNTs and the quartz substrate does not contribute to the photon-pair generation.

**Figure 5.6.** The experimental setup for generating and characterizing photon pairs in SWNTs. A stimulated FWM experiment is also shown, where a dichroic mirror is inserted after the fiber collimator to couple an idler probe beam at 1555.68 nm. The dichroic mirror is removed when we perform photon-pair generation experiment (i.e., no input beam at 1555.68 nm). In this case, two pump photons scatter through the Kerr-nonlinearity in SWNTs and create an energy-time entangled signal-idler photon pair at the wavelengths of 1544.56 and 1555.68 nm. WDM1, WDM2, WDM3, and WDM4: wavelength-division multiplexing filter; EDFA: Erbium-doped-fiber-amplifier; QWP1 and QWP2: quarter-wave plate; HWP1 and HWP2: half-wave plate; PBS: polarizer beam splitter. APD1 and APD2: avalanche photodiode. [Publication V]

The conversion efficiency of stimulated FWM process in the SWNT had a quadratic dependence on power, as shown in Figure 5.7. With this stimulated FWM process, we can estimate various nonlinearities (nonlinear refractive index $n_2$, parametric nonlinearity $\gamma$, and Raman gain
By fitting the plots in Figure 5.7 with a quadratic polynomial function of pump power ($P_p$), $m_0+m_1P_p+m_2P_p^2$, we obtained the Raman gain coefficient ($m_1$) and nonlinear refractive index ($m_2$) of the SWNT film and the quartz reference. The detailed calculation on these nonlinear optical parameters can be found in Publication V. And the results showed that the nonlinear refractive index of the SWNT as $n_{SWNT}^2 \approx (1.27 \pm 0.21) \times 10^{-14} \text{m}^2 \text{W}^{-1}$, which was around five orders of magnitude higher than the reference fused quartz ($n_0^2$). Considering the effective area of $\approx 80 \mu \text{m}^2$, we obtained the nonlinear parameter $\gamma_{SWNT} \approx (6.4 \pm 1.1) \times 10^{5} \text{ W}^{-1} \text{km}^{-1}$, which was about $3 \times 10^5$ times larger than silica fibers [184]. This indicates that SWNTs have great potential for classical and non-classical light generation through nonlinear optical processes.

![Figure 5.7.](image)

**Figure 5.7.** The ratio of $P_s/P_i$ and the conversion efficiency for the SWNT device in the stimulated FWM process. The solid line is the fitting curve. The dashed line is the fitting curve for the quadratic component only. Inset is the ratio of $P_s/P_i$ for the reference fused quartz device. [Publication V]

Then we tested the SWNT thin film for photon pair generation. We measured the coincidence and accidental counts as a function of pump power for the SWNT device and the fused quartz reference sample. After subtracting the contribution from the fused quartz, we obtained the coincidence, accidental and true coincidence for the thin layer of pure SWNTs as shown in Figure 5.8 (a). We then plotted the coincidence to acciden-
We observe a maximum CAR of 15 for the SWNT film on the fused quartz substrate. After the subtraction of the coincidences and accidentals from the reference fused quartz, we obtained the maximum CAR of 18 for the pure SWNT film. The maximum CAR occurred at the peak pump power $\approx 5.3 \text{ W}$, and we had coincidence counts (cc) of 54 and accidental counts of 3 within the integration time of 1.7-min. Note that the true coincidence was $54 - 3 = 51 \text{ cc}$, which was the contribution from photon pairs generated through spontaneous FWM process. Considering the total detection efficiency (about 0.5% for the signal, 0.6% for the idler), we had $51/(0.6\% \times 0.5\%) = 1\,700\,000 \text{ cc per 1.7-min.}$ This corresponded to $\approx 16\,667 \text{ photon pairs per second with our carbon nanotube device.}$ Since we used the pump laser with the repetition rate of 50 MHz, we have the photon-pair production rate of $P_r \approx \frac{16667}{50 \times 10^6} \approx 3.3 \times 10^{-4}$ per pulse, comparable to these photon-pair sources based on photonic crystal fibers [201–205]. Note that SWNTs are compatible with the existence optical fiber network for developing long distance quantum communication.

Our results indicate that nanoscale SWNT devices are a promising nonlinear nanomaterial suitable for manipulating and generating light for quantum information processing at the nanoscale level. Further studies on photon-pair generation in isolated SWNTs (or a free-standing SWNT film) and other low dimensional nanomaterials (e.g., graphene, other 2D nanomaterials) with high-nonlinearity can potentially lead to the demonstration of nanometer-scale sources for integrated quantum circuits and networks.

Figure 5.8. (a) The coincidence (circle), accidental (square), and true coincidence (triangle) for the signal and idler generated in SWNTs as a function of pump power per 1.7-min. (b) The CAR for the pure SWNT nanofilm only (i.e., after subtracting the contribution from the fused quartz substrate) as a function of pump peak power. The coincidence, accidental, and CAR were reported with the subtraction of detector dark counts. [Publication V]
CNTs based linear and nonlinear photonic devices
6. Nanowires based all-optical logic gates

Due to the structural confinement and large ratio between the length and the diameter of NWs, the optical responses (e.g., PL \cite{9}) from NWs are extremely sensitive to the excitation light polarization direction. Based on this optical property, we fabricate a polarization controlled all-optical switch with sub-wavelength dimensions by preparing a crossbar network using InP and AlGaAs NWs. Furthermore, the NW structures can work as various logic gates to perform arithmetic calculations (e.g., adder and multipliers). In this chapter, the anisotropic optical PL property and the realization of multifunctional all-optical logic gates are presented.

6.1 Polarization dependent photoluminescence property

In the chapter IV, we have presented the method of preparing aligned crossbar NW junctions (details in Publication III). Here, we introduce their PL emission property as a function of the excited laser polarization direction. As shown in Figure 6.1(a), 6 pairs of well-aligned InP and AlGaAs crossbar NW junctions were found in such a $\sim 6 \times 6 \, \mu m^2$ area, one of which was selected as an example to test the room temperature PL. The measurement was taken from a single spot with the excitation wavelengths at 532 nm and 730 nm, respectively. The PL measurement results were shown in Figure 6.1(b).

Figure 6.1(b) clearly showed that there were two PL peaks located at the wavelengths of 665 nm and 890 nm under the 532 nm laser excitation, which were attributed to AlGaAs and InP NWs, respectively. While, only a single peak appeared at the wavelength of 890 nm under the 730 nm laser excitation because the photon energy of the excitation laser was lower than the bandgap of AlGaAs NW. To explain the origin of the PL peaks, the structural analysis from both two NWs were examined.
Figure 6.1. Nanocombing of InP and AlGaAs crossbar NW networks and their optical emission properties. (a) SEM image of the crossbar NW network; InP NWs are combed along the vertical direction and AlGaAs NWs along the horizontal direction. (b) PL spectra of the NWs measured at a single exemplary measurement spot using an excitation laser of 532 nm and 730 nm with vertical and horizontal polarization directions. (c) HRSTEM image of InP NWs. The inset shows the diffraction pattern demonstrating the zincblende crystal structure and formation of frequent twin planes along the NW growth axis. (d) EDX measurement results of AlGaAs NWs show the Al and Ga composition along the NW growth direction (i.e., [111] crystal direction). The linescan location is shown in the inset. [Publication III]

by high-resolution scanning transmission electron microscopy (HRSTEM) and energy-dispersive X-ray (EDX) measurements. The detailed discussions on their transmission electron microscopy (TEM) were presented in the publication III. Here, we mainly focused on their PL emission property under different excitation polarization directions.

Figure 6.1 (b) showed the relative magnitude of the PL peaks depended on the polarization direction of the excitation laser. When the polarization direction of the 532 nm excitation laser was parallel to the AlGaAs NW growth axis, the PL signal emerged at the wavelength of 665 nm.
However, when the laser polarization direction was parallel to the InP aligned direction, the PL signal was observed at the wavelength of 890 nm. This was due to the intrinsic anisotropic structure of NWs. We also calculated DOP (DOP = \( \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}} \)) of the PL intensities from the InP and AlGaAs NWs to be 94% and 65%, respectively. Thus, by rotating the laser polarization direction, the crossbar NW junction could emit PL at different wavelengths. This phenomenon was easily observed at the sub-wavelength dimension originating from their linear optics, which showed their great potential in future on-chip nanophotonics.

### 6.2 All-optical logic gates

Based on the above results of the polarization controlled PL wavelength switch, all-optical nanoscale NAND and NOR logic gates were constructed and presented in this section. The key part for the functionalities was the crossbar InP and AlGaAs NW junction as shown in Figure 6.1(a), which thanks to the large-scale combing method without any lithography process (see methods in Chapter IV). The truth tables of our proposed all-optical NAND and NOR logic gates are illustrated in Figure 6.2. For NAND logic gate, the input state of the gate was coded in the excitation light wavelength (i.e., \( A_i \)) and the polarization direction (i.e., \( B_i \)), and the output was defined by the PL signal from the NW junctions (i.e., \( c_{ij} \), with \( j = 1 \) implying NAND function). Thus the NAND operation was realized by defining the gate output as the PL signal at the wavelength range covering the band gaps of AlGaAs and InP, while simultaneously excluding the excitation laser wavelengths (i.e., \( \lambda_{PL} \in [620 \, \text{nm}, 690 \, \text{nm}] \land [860 \, \text{nm}, 940 \, \text{nm}] \)). In case PL signal emerged in this wavelength range, NAND gate

![Figure 6.2](image)

**Figure 6.2.** The truth tables of NOR and NAND logic gates using the polarization dependent PL property of NWs. The inputs are labeled by \( A_i \) and \( B_i \), and the output is coded as \( C_{ij} \) by different logic function, where \( j = 1, 2 \) implying NAND and NOR function, respectively.
Nanowires based all-optical logic gates returned an output of 1. Therefore, an output of 0 was only obtained if the gate was excited by the 730 nm wavelength with the polarization direction along AlGaAs NWs (corresponding to the input state of $A_i=1$ and $B_i=1$). While for NOR gate, the input was coded similarly in the excitation laser wavelength ($A_i$) and their corresponding polarization direction ($B_i$), where the definition of the polarization direction was opposite to that of NAND logic operation. And the output was defined by the PL signal only from AlGaAs NWs (i.e. $c_{ij}$ with $j=2$ for NOR function). For instance, the gate output of 1 was defined as PL signal at the wavelength range covering the band gap of AlGaAs growth direction (i.e., $\lambda_{PL} \in [620 \text{ nm}, 690 \text{ nm}]$). Otherwise, NOR gate returned an output of 0. Due to this definition, the gate returned a value of 1 only when 532 nm laser excitation and the polarization direction along the aligned direction of AlGaAs NWs (corresponding to the input state of $A_i=0$ and $B_i=0$). It was noteworthy to mention that by defining our NW based logic gate output similarly but the input differently, the NW junction can also be used for OR and AND all-optical logic functions.

### 6.3 Arithmetic all-optical applications

After the construction of the above logic gates, the arithmetic calculation application was presented in this part. To simplify the situation, we firstly explained how the results of 1-bit addition operation can be read from the gate outputs. In case $1_2$ was added to $1_2$ (with subscript 2 defining the number as binary number), the inputs of NAND and NOR gates (i.e., $A_1=1$ and $B_1=1$) returned outputs of $c_{11}=0$ and $c_{12}=0$, respectively. On the other hand, if $0_2$ was added to $1_2$ (or $1_2$ to $0_2$), the gate inputs of $A_1=0$ (or 1) and $B_1=1$ (or 0) returned output values of $c_{11}=1$ for NAND logic gate and $c_{12}=0$ for NOR logic gate. Furthermore, the NAND and NOR logic gates only returned a value of $c_{11}=1$ and $c_{12}=1$ when both inputs were 0 (i.e., gate inputs of $A_1=0$ and $B_1=0$). As a result, three different gate output configurations were possible in two 1-bit addition operations, and therefore, the result (i.e., $D = D_2D_1$) of the addition operation can be unambiguously obtained from the gate outputs. By following the same order as above, the gate output configurations returned a result of $D = 10_2$, $D = 01_2$ and $D = 00_2$ for addition operation of two 1-bit numbers, as shown in Figure 6.3. More complex situation was conducting an addition operation of two n-bit numbers (A and B as above), since the possibility
of the carry information needed to be taken into consideration, which still can be obtained by following the rules in Figure 6.3.

<table>
<thead>
<tr>
<th>1st bit</th>
<th>n'th bit</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{11}</td>
<td>C_{n1}</td>
</tr>
<tr>
<td>C_{12}</td>
<td>C_{n2}</td>
</tr>
<tr>
<td>D_{1}</td>
<td>Carry_{n}</td>
</tr>
<tr>
<td>Carry_{1}</td>
<td></td>
</tr>
</tbody>
</table>

![Table](image)

Figure 6.3. The rules on how to read out the addition operation result from NOR and NAND logic gate outputs. The below box is an example of two 5-bit numbers addition. [Publication III]

Figure 6.4. PL mapping shows how one all-optical NW logic gate operates when 24 (11010₂) is added to 16 (01110₂). [Publication III]

To verify the function of NW junction based logic gates, an example of the logic gates outputs, expressed by the PL mapping results, was presented in Figure 6.4 with an addition operation of two 5-bit numbers (11010₂ + 01110₂). As clearly shown in PL maps of NAND gate, PL signal (threshold value for PL ~ 0.3) emerged with the (0,0), (1,0) and (0,1) gate inputs; while only for (1,1) input no PL signal was created. This was in agreement with our proposed all-optical NAND function (described above). The operation of NOR gate was demonstrated similarly. As shown in Figure 6.4, PL signal (threshold value for PL ~0.6) was generated only when the NOR gate input was (0,0). Since all other gate inputs returned a gate output value of 0, the realization of the NOR function was experimentally confirmed. The result of the exemplary addition operation can

43
also be checked by following the rules in Figure 6.3 with the final carry information placed as the largest bit. Besides the addition operation, the subtraction can also be realized with considering the largest bit as the sign of the number.

**Figure 6.5.** NWs based all-optical 2-bit multiplier. (a) The optical image of vertically combed InP NWs. The dashed white-boxes highlight the locations where 4 parallel AND logic gates are constructed. (b) The truth table of AND logic gate using the polarization dependent PL property of InP NWs (the A<sub>i</sub> and B<sub>i</sub> input bits are coded in the laser state (on or off) and the excitation laser polarization direction (horizontal (H) or vertical (V), respectively) and the rules on how to read out the multiply result from the gate outputs.

<table>
<thead>
<tr>
<th>Input</th>
<th>Output</th>
<th>C&lt;sub&gt;11&lt;/sub&gt;</th>
<th>C&lt;sub&gt;12&lt;/sub&gt;</th>
<th>D&lt;sub&gt;1&lt;/sub&gt;</th>
<th>D&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Carry&lt;sub&gt;2&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>A&lt;sub&gt;i&lt;/sub&gt;</td>
<td>B&lt;sub&gt;i&lt;/sub&gt;</td>
<td>C&lt;sub&gt;i&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 (off)</td>
<td>0 (H)</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
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<td>1 (V)</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>1 (on)</td>
<td>0 (H)</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1 (on)</td>
<td>1 (V)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Figure 6.6.** Three exemplary calculations, (3×3 (i.e., 11<sub>2</sub>×11<sub>2</sub>), 3×2 (i.e., 11<sub>2</sub>×10<sub>2</sub>), and 2×3 (i.e., 10<sub>2</sub>×11<sub>2</sub>), respectively, showing the gate outputs and demonstrating how the multiplication operation result is obtained from the PL maps.

In addition, multiplication operation was also realized with the NW junctions. In this case, only aligned InP NWs were needed, which were shown in Figure 6.5 (a). In our design, four parallel AND gates were employed to execute the two 2-bit multiplication operation, and the truth table was shown in Figure 6.5 (b). The definition for the input and output in our case were described as: the input states were defined as the excitation light power (i.e., A<sub>i</sub>) and the polarization direction (i.e., B<sub>i</sub>) were defined as the input states, and the InP PL intensity (i.e., c<sub>ij</sub>) was defined as the gate output value. Based on this definition, the aligned InP NWs emitted
PL (i.e., creating a gate output of 1) only when the excitation laser was on and the polarization direction was along InP NW growth axis. In all the other cases, no PL was observed, corresponding to a gate output value of 0. The rules for the two 2-bit multiplication operation resulted from the output of four AND gates were listed in Figure 6.6. By applying the rules to the PL maps of four parallel AND gates, the multiplication results of three exemplary calculations were obtained. Thus, the aligned NW structure successfully realized the operation of 2-bit multiplier calculations by all-optical method.

In summary, we demonstrate a novel method to construct a nanoscale all-optical wavelength switch based on the polarization dependent PL properties of the crossbar InP and AlGaAs NW networks. The structure is formed without any lithography process by combing InP and AlGaAs NWs along the two perpendicular directions, allowing the emission wavelength of the crossbar structure to be tuned over 200 nm by modulating the excitation laser polarization direction. This polarization-controlled behaviour allows the fabrication of multiple parallel all-optical logic gates with sub-wavelength dimension. By using the fabricated multifunctional all-optical logic gates with AND, OR, NAND and NOR functions, our structure successfully enables the light to perform the binary arithmetic operations such as n-bit addition. Overall, our results underscore that such a NW network is an interesting candidate for future all-optical nanophotonic devices. In particular, the reported NW building block provides a scalable alternative to be used in the future all-optical nanoprocessor circuits.
Nanowires based all-optical logic gates
In addition to the above mentioned 1D materials, 2D materials also show anisotropic linear and nonlinear optical properties for various photonic applications. In this chapter, we discuss the anisotropic properties of BP based on its asymmetric structure. Because of its birefringence, the application of BP as an optical waveplate in the visible range is demonstrated. Another two anisotropic 2D materials (ReS$_2$ and ReSe$_2$) are also studied for their waveplate applications.

7.1 BP based waveplates

Birefringence is an inherent optical property of anisotropic materials introduced by the anisotropic confinement in their crystal structures. It enables manipulation of light propagation properties (e.g., phase velocity, reflection, and refraction) for various photonics and optoelectronics, including waveplates and liquid crystal displays. 2D layered materials with high anisotropy are currently gaining an increasing interest for polarization-integrated nano-device applications, which advances the research on birefringent nanomaterials. Compared to other anisotropic 2D layered materials, BP is highlighted because of the layer-dependent direct band gap and its in-plane anisotropy stemming from its unique atomic-puckering crystal structure [85, 99]. Its special band gap (ranging from 0.3 to 1.5 eV [94]) and anisotropic absorption property make it an ideal candidate as a promising optical polarizer in a wide spectrum window.

In this part, the birefringence of BP is mainly discussed. Based on the birefringence, the waveplate performance of BP is also presented. For comparison, the birefringence of another two anisotropic materials (ReS$_2$ and ReSe$_2$) is examined and presented. The comparison results show BP has a larger birefringence and offers better performance over other two
anisotropic 2D materials (i.e., ReS$_2$, ReSe$_2$).

### 7.1.1 Anisotropic properties of BP

The structure of bulk BP has an orthorhombic symmetry belonging to the point group $D_{2h}^1$ (Cmca) [99], with four atoms per unit cell, as shown in Figure 2.5. BP has a puckered layered structure with strong anisotropy in the basal plane, which is reflected by its physical properties [90, 97]. Polarized Raman spectroscopy illustrates the complete angular-dependent Raman scattering. From the fitting curve of the angular dependence of different Raman mode intensities, we could identify the crystal orientation of BP crystal, with detailed discussion in Publication II.

For BP crystals, there are mainly three Raman modes at 363, 440, and 468 cm$^{-1}$, corresponding to $A^1_{g}$, $B^2_{2g}$, and $A^2_{g}$ vibration modes, respectively. The intensity of a given Raman mode, which is related to the Raman tensor and scattering geometry, is proportional to the expression $|e_i \cdot \tilde{R} \cdot e_s|^2$ [206], where $e_i$ means the incident laser polarization, $\tilde{R}$ means the Raman tensor of different modes, $e_s$ means the scattering radiation direction. According to the generalized form of Raman tensors [103], the intensities of $A_g$ and $B_{2g}$ Raman modes are closely related to the sample rotation angle $\theta$ under both the parallel and cross-polarization configurations. With the rotation of the crystal orientation from $0^\circ$ to $360^\circ$ under both two configurations, the variation features of these modes are shown in Figure 7.1 (a-f). It can be clearly seen that different Raman modes showed different periodic variation features. Under parallel polarization configuration, the $A^1_{g}$ mode intensity showes a $180^\circ$ variation period. The $A^2_{g}$ mode showes a $90^\circ$ variation period, which reaches the local maximum at $\theta = 0^\circ/90^\circ$. There are two different local maxima for the $A^2_{g}$ mode, which is attributed to the different values in the Raman tensor. Furthermore, the intensity of $B_{2g}$ mode is proportional to $\sin^2(2\theta)$ with $90^\circ$ variation period, which achieves the maximum at $\theta = 45^\circ$ and is completely forbidden at $\theta = 0^\circ/90^\circ$. The case is different under the cross-polarization configuration: the intensities of all three Raman modes exhibites $90^\circ$ variation period with the sample rotation angle $\theta$. From these results we can see that with the crystalline orientation (zigzag (ZZ) or armchair (AM) direction) along the polarization direction of the scattered light, the intensity of these Raman modes reache a local maximum or minimum value, which is consistent with the scattering efficiency based on their Raman tensors. These results further examine the optical anisotropy nature of BP. And
more importantly, according to the intensity variation of the $A_2^g$ mode under parallel polarization configuration, the crystal orientation can be identified. In our results, shown in Figure 7.1(b), the AC direction of this BP sample was parallel with the direction of the excitation laser polarization when the BP flake was rotated by $90^\circ$ (or $270^\circ$).

To determine the anisotropy of BP, PROM images were taken. In general, under the cross-polarization configuration of the PROM, light did not transmit through, which gave the dark optical images. But inserting an anisotropy crystal between the polarizer and the analyzer, the state of the polarized light changed, causing the light to pass through. When the optical axis of the crystal was placed between the polarizer and analyzer at an angle of $\theta$ corresponding to the polarizer direction, the intensity of the transmitted light was expressed as

$$I(\theta) = I_0 \sin^2(2\theta) \sin^2(\delta/2)$$

(7.1)

where $I(\theta)$ was the transmitted light, $I_0$ was the transmitted light under parallel configuration, $\delta$ was the retardance. With this equation, the change in brightness during the rotation of the anisotropic crystal and the interference colour from retardation can be explained.

The PROM images of a BP flake as a function of the flake rotation angle under cross-polarization configuration were illustrated in Figure 7.2. It
mainly presents three colours—green, yellow and purple (marked with different dotted boxes), originating from the interference effect on the flake with different thicknesses [207]. As clearly seen, the flake brightness appeared the highest when the crystal orientation was 45° (and 135°) with respect to the incident polarization direction, while no contrast from the BP flake was observed when one of the crystal axes was parallel to the polarizer direction (i.e., 0° and 90°). This phenomenon was consistent with the above explanation, which originated from the birefringence of BP crystal. At the same time, the flake colours at different flake thicknesses were different under the same measurement conditions.

![Figure 7.2. Transmitted polarization-resolved optical images under crossed-polarized light illumination in the PROM (i.e., the polarization direction of the incident light and the polarization analyser was perpendicular to each other) with the BP flake rotation angle from 0° to 165°. The step of rotation angle was 15°. [Publication II]](image)

In addition to the PROM images, the quantitative transmitted-light intensity was measured as a function of the flake rotation angle. The result was shown in Figure 7.3. As shown, the intensity changed periodically with the flake rotation angle with a period of 90°. In particular, the transmitted intensity was the lowest when the BP flake was rotated by 0° and 90°. When the flake was rotated by 45° with respect to the incident light polarization, the transmitted light intensity through the BP flake was the highest. The red line was the fitting following Eq 7.1. These results highlighted the intrinsic optical birefringence of the anisotropic BP crystals.

### 7.1.2 Birefringence of BP

To quantitatively characterize the birefringence of BP, we measured the phase shift (i.e., the phase retardance) between two polarization components projected along two different crystallographic orientations when a linearly-polarized beam passed through the flake; see the schematic diagram in Figure 7.4. We used a custom-built setup to quantitatively characterize the birefringence of the anisotropic materials. In this figure, BP
Figure 7.3. The light transmittance as a function of BP flake rotation angle under crossed polarization illumination. The red line depicted the fitting result. [Publication II]

was illustrated here as an example, and other anisotropic materials can also be checked to examine their birefringence. The input laser was adjusted to be nearly-linearly polarized with the help of a Glan–Thompson prism. The input polarization direction had an angle $\theta$ with the crystal axis (e.g., ZZ axis of BP). After transmitting through the flake, the output polarization state was examined through a polarization analyzer (another polarizer). By rotating the polarization analyzer, the maximum ($I_{\text{max}}$) and minimum ($I_{\text{min}}$) output light power was recorded by a power detector to analyze the polarization state of the output light. In this case, $I_{\text{max}}$ standed for the intensity along the long-axis (e.g., ZZ direction), while $I_{\text{min}}$ for the short-axis (e.g., AC direction). Therefore, the polarization ellipticity ($e$) of the light passing through the flake can be calculated by the intensity ratio between the long and short axis (i.e., $e=I_{\text{max}}/I_{\text{min}}$) for birefringence characterization.

Here, I listed the ellipticity change as a function of the flake rotation angle ($\theta$) after the light passes through a $\sim 45$ nm thick BP flake at three different wavelengths (e.g., 520 nm, 642 nm, and 730 nm), shown in Figure 7.5 (a). It can be seen that the ellipticity is changed with the rotation of the flake, resulting from the birefringence of BP crystal. To obtain the value of birefringence, the ellipticity change is numerically fitted based on the equation

$$\sqrt{e} = \frac{1 + s\sqrt{1 - 4\sin^2(\theta)A_{zz}^2A_{AC}^2/(A_{zz}^2+A_{AC}^2)^2}}{1 - s\sqrt{1 - 4\sin^2(\theta)A_{zz}^2A_{AC}^2/(A_{zz}^2+A_{AC}^2)^2}} \quad (7.2)$$
where \( s = 1 \) for \( A_{ZZ}^2 - A_{AC}^2 \geq 0 \), and \( s = -1 \) for \( A_{ZZ}^2 - A_{AC}^2 < 0 \). \( A_{AC} \) and \( A_{ZZ} \) were the amplitude of the transmitted light projected along the AC and ZZ directions, respectively, with the consideration of \( \theta \) and the transmission coefficient along the AC and ZZ crystal axes separately. \( \delta \) was the phase retardance between the AC and ZZ axes after light propagating through BP flakes. In our model, the incident light was normal to the flake surface, and the dichroic absorption was also considered in the fitting. From the fitting, we could get the phase retardance caused by the birefringence of the crystal. In theory, the phase retardance is expressed by the equation

\[
\delta(d) = \frac{2\pi \times \Delta n}{\lambda} d + \delta_0
\]

(7.3)

\( \delta(d) \) is related with the light wavelength, the crystal thickness and the birefringence value. As the material birefringence was independent of the material thickness, we examined more flakes with different thicknesses at 45 nm, 70 nm, 100 nm, and 220 nm. Then by fitting the phase retardance as a function of the flake thickness using Equation 7.3, the birefringence value was obtained. The birefringence of BP at three wavelengths was illustrated in Figure 7.5 (b). For comparison, the theoretically calculated data was plotted as well for comparison, which was matched well with the experimental data.

### 7.1.3 Waveplate performance of BP

Anisotropic bulk crystals (e.g., CaCO\(_3\), LiNbO\(_3\)) are excellent candidates for waveplates to manipulate the polarization state of the light because of their birefringence. However, with the development of integrated nanophotonic devices, integrated polarization-controllers at the nanoscale are
highly required. BP is an anisotropic nanomaterial with large birefringence, which is suitable for nanoscale waveplate applications. In Publication II, the waveplate performance of BP is described in the view of the rotation of the polarization-plane of the incident light. For comparison, the waveplate performance of ReS$_2$ and ReSe$_2$ is also presented.

As shown in Figure 7.4, the angle $\phi$ describes the rotation angle of the incident light’s polarization-plane caused by the birefringence. Figure 7.6 presents the experimentally measured maximum $\phi$ as a function of the flake thickness at three wavelengths (e.g., 520, 642, and 730 nm, respectively). As illustrated, $\phi$ increased with the flake thickness, as the optical path length was longer in the thicker flakes at a certain wavelength. However, as observed from the flakes with different thicknesses, $\phi$ at 520 nm wavelength was larger than that at 642 nm and was the smallest at 730 nm wavelength. The maximum $\phi$ at 520 nm wavelength was 21° for the 220 nm thick flake, corresponding to the polarization rotation angle of $\sim$0.05° per atomic layer with the monolayer thickness of 0.53 nm [208]. As $\Delta n$ is wavelength dependent, indicating the chromatic dispersion of BP. This explains the wavelength dependence of $\phi$ in Figure 7.6.

### 7.2 ReS$_2$ and ReSe$_2$ based waveplates

In addition to BP, ReS$_2$ and ReSe$_2$ are 2D anisotropic nanomaterials arising from their crystal lattice asymmetry, which gives rise to their anisotropic electronic structure and physical properties. Different from BP with poor environmental stability, ReS$_2$ and ReSe$_2$ have low-symmetry distorted 1T structures with excellent stability. Based on their anisotropic structures,
we experimentally explored their birefringences and the modulation property for the light polarization.

In my Publication II, the optical birefringence phenomenon of ReS$_2$ and ReSe$_2$ was examined by polarization optical microscopy and polarization Raman microscopy. Their birefringences were characterized using the same method as BP. Figure 7.7 shows the experimental results of the birefringence of ReS$_2$ and ReSe$_2$, which is wavelength dependent but the difference between them is small. We propose that this is because the atomic structures and properties of ReS$_2$ and ReSe$_2$ are similar [209].

Similarly, the rotation angle of the polarization-plane as a function of the flake thickness of ReS$_2$ and ReSe$_2$ at the three wavelengths was also studied, shown in Figure 7.8. The trend was the same as BP for the re-
lation between the $\phi$ and the flake thickness, but the relation with the wavelength was not so clear as their birefringence difference was quite small, which originated from their similar crystal structures and physical properties. By comparing Figure 7.6 to Figure 7.8, $\phi$ of ReS$_2$ and ReSe$_2$ was much smaller than that from BP, which showed that BP offers better polarization control performance than ReS$_2$ and ReSe$_2$ crystals.

**Figure 7.8.** The maximum polarization-plane rotation angles ($\phi$) as a function of (a) ReS$_2$ and (b) ReSe$_2$ flake thickness in the visible wavelength. [Publication II]
2D materials based waveplates
8. Summary and Outlook

The optical properties of various low-dimensional nanomaterials (i.e., CNTs, NWs, BP, ReS$_2$ and ReSe$_2$) with anisotropic structures are studied in this thesis. The reasons for their anisotropic optical responses are different. ACNTs and NWs have 1D quantum confinement, which leads to their anisotropic optical responses, but the optical responses of 2D anisotropic materials arise from their intrinsic asymmetry crystal structures. Overall, all of them show obvious anisotropic optical responses, and they have been applied into different optical systems for polarization control.

For 1D nanomaterials, ACNTs were firstly introduced. The Raman mode scattering intensity was measured to check the alignment of the CNT device. Polarized Raman spectra were obtained by changing the input polarization direction from $0^\circ$ to $360^\circ$ with respect to the CNT alignment direction. It was found that the ratio between the maximum and the minimum G-peak intensity was $\sim 22$, which clearly showed the polarized absorbance of the ACNT device. The polarized absorption spectrum was measured using a polarized absorption/transmission spectroscopy. The results illustrated that the absorption difference between two orthogonal directions (parallel and perpendicular to the CNT aligned direction, respectively) was $\sim 12\%$ at 1.8 $\mu$m, and $\sim 16\%$ at 300 nm, which was comparable to the typical performance of the previously reported ACNT devices. In addition, the transmittance difference remained almost constant from 1 to 2 $\mu$m, which illustrated the unique broad operation bandwidth of the ACNT device. After characterizing the broadband anisotropic absorption properties, the ACNT device was inserted into fiber laser systems (at 1 and 1.5 $\mu$m, respectively) to control the laser output polarization. The laser output was examined to be linearly polarized with the DOP at 89.1\% and 87.5\% (the corresponding ER of 12.4 and 12 dB) at 1 and 1.5 $\mu$m laser systems, respectively. The results exhibited that the ACNT de-
vice could be used as polarization controller in a broad range of photonic applications.

Individual NWs also possess large aspect ratio between the length and the diameter, leading to their anisotropic absorption along two orthogonal directions. Firstly, a top-down nanocombing method was used to align the randomly pointing NWs in the horizontal plane, and the statistics showed that 95\% of the NWs was aligned along one direction. By using the dry-transfer method, the building blocks with crossbar InP and AlGaAs NW junctions were successfully prepared. To study the anisotropic responses from the NW, the polarization PL property was studied by rotating the polarization of the excitation laser. Different PL wavelengths appeared from the building blocks under different polarization directions of the excited laser. Based on this wavelength intensity switch property, these crossbar NW building blocks were designed to be various logic gates (e.g., AND, OR, NAND and NOR) by defining the excitation wavelength and polarization. Based on these constructed logic gates, the arithmetic calculations (addition and multiplication) were demonstrated, which exhibited great potential applications of NW-based building blocks as nano-processors in the on-chip all-optical circuits.

For 2D materials, we mainly introduced BP as an example to study the birefringence and the corresponding waveplate applications, as the same birefringence measurement method can be used for various kinds of anisotropic 2D layered materials. In this part, we introduced two ways to determine the crystal orientations, polarized Raman microscopy and PROM. Compared with polarized Raman method, PROM was faster and easier, as the polarized optical image can directly show the crystal axis orientation. In addition, for some anisotropic nanomaterials with lower-symmetry, PROM method was a better choice for crystal orientation determination. After determining the crystal orientations, a custom-built polarized optical microscopy was used to measure the birefringence of BP. By fitting the ellipticity change of the transmitted light with the rotation of the crystal orientation, the birefringence of the BP was obtained, matching well with the theoretically calculated results. Using the same measurement method, the birefringence of ReS$_2$ and ReSe$_2$ was also examined, which was 6 times smaller than that of BP. The results show that the birefringence of BP is comparable to that of bulk commercial anisotropic materials (e.g., CaCO$_3$).

One of the important optical applications of the anisotropic materials
was waveplate. In this work, BP’s waveplate performance was examined in view of the polarization-plane rotation angle of the linearly polarized input light. The results showed that BP with one atomic layer (∼0.7 nm) at 520 nm could cause the rotation angle of 0.05°, which gave better polarization control performance than ReS₂ and ReSe₂. The results highlighted the relatively large birefringence of anisotropic 2D materials, such as BP, can facilitate accurate manipulation of light polarization with atomically controlled device thickness.

Except the linear photonic applications of the above mentioned nanomaterials, their part of non-linear photonic applications were also illustrated. For example, FWM from CNTs was used for photon-pair generation. This demonstration shows their great potential in the future nonlinear photonic applications.

In this thesis, the anisotropic optical properties of three different kinds of nanomaterials were studied, which showed great polarization control performance in various optical devices and systems. Except the three materials mentioned here, there are still many other 1D materials (e.g., nanorods, nanoribbons), and 2D materials (e.g., SnS, SnSe, InSe) with similar or better anisotropic properties. In addition, various patterned 2D materials and their heterostructures (e.g., graphene nanoribbons [210–212], MoS₂ [78, 213–216] ribbons), their intrinsic anisotropic properties (e.g., birefringence, absorption), and their anisotropy-based photonic applications deserve further investigation (e.g., nonlinear optical devices [88], photodetectors, sensors, ultrafast lasers [217], solar cells, waveguides [218]). It is also interesting to try to modulate their anisotropic optical properties (e.g., by external electric [68], magnetic field, or strain [219]) and integrate them with various hybrid photonic systems (e.g., fiber [24], silicon waveguides [220, 221], plasmonic structures [222, 223] and bio-materials [224]) for various optoelectronic applications.
References


