

Planar Microcavity-enhanced Lasing from Semiconducting Carbon Nanotubes

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

Single-walled carbon nanotubes (SWCNTs) exhibit exceptional optical properties, including strong oscillator strength, size- and chirality-dependent tunable bandgap energies, and near-infrared (NIR) photoluminescence (PL) at room temperature. These features make them highly attractive and promising candidates for a wide range of optoelectronic and quantum optical applications. However, their practical deployment has been significantly hindered by several challenges such as PL quenching due to nanotube bundling, structural degradation from high-temperature annealing, or internal loss mechanism of exciton-exciton annihilation (EEA) under high excitation power. To overcome these challenges and enhance the radiative efficiency of SWCNTs, we design and fabricate wafer-scale dielectric distributed Bragg reflectors (DBR) to construct high-quality Fabry-Perot (FP) planar microcavities, where thin films of chirality-sorted, well-dispersed SWCNTs. These cavities serve to promote strong light-matter coupling between confined cavity photons and excitons in the SWCNT films.

We perform optical characterization of the SWCNT-embedded microcavity devices both in weak and strong light-matter coupling regimes. First, in the strong coupling regime, we observe the SWCNT exciton-polariton dispersions with vacuum Rabi splitting (VRS) strength around 210 meV. Unfortunately, the polariton condensation was not achieved, primarily due to internal material loss mechanisms such as EEA process or strong reabsorption. On the other hand, we observe nonlinear lasing behavior in weak light-matter coupling regime, evidenced by a pronounced spectral linewidth narrowing signature with increasing excitation power. This would represent the first demonstration of lasing from SWCNT thin films integrated into planar dielectric microcavities, marking a significant milestone in carbon-based nanophotonics. While the results are promising, there remains considerable scope for enhancing the coherence and quality of the emitting light from these SWCNT-embedded microcavity devices, an essential step toward realizing scalable quantum nanophotonic platforms.

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Finally, I wish to convey my deepest and most heartfelt appreciation to my parents, my wife's parents, and especially to my wife and children, whose unwavering love, steadfast support, and continuous encouragement have been my greatest source

of strength throughout the entirety of my academic journey. Their patience, sacrifices, and belief in me have sustained me through the challenges of research and writing, and this achievement would not have been possible without their constant presence by my side. I am forever grateful to them for their immeasurable contributions to both my personal and academic life.

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Dedication

To Prof. Kim, whose extraordinary mentorship kindled my passion for research and showed me that it is never too late to follow one's true calling.

To my beloved family, my parents, my wife's parents, my wife, and my children, whose unwavering love, support, and encouragement have been the foundation of all my endeavors and the source of my strength.

This work is dedicated to you all.

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List of Abbreviations

- 1D** one-dimensional 2, 28, 30, 34, 39, 45–47, 49, 108, 109, 116, 117, 119, 125
- 2D** two-dimensional xii–xiv, xvi–xviii, 2, 12, 13, 18, 28–30, 34, 38, 43, 47, 87, 92, 108–110, 112–120
- 3D** three-dimensional xiii, 18, 28–30, 44, 83
- ATPE** aqueous two-phase extraction xv, xvi, 3, 4, 56, 63, 66–68, 70, 83, 86–88, 122, 151
- BCB** benzocyclobutene xvii, 89, 102, 103, 112–114, 116, 118
- CNT** carbon nanotube 2, 27, 30, 32–34, 36, 38, 39, 57, 62, 63, 158
- CVD** chemical vapor deposition 3, 38, 54, 60, 62, 158
- DBR** distributed Bragg reflector xiii, xiv, xvi–xviii, 4, 12, 24–27, 53–55, 57–61, 92, 95, 96, 98–106, 113–115, 117, 119–123
- DEP** dielectrophoresis 83
- DGU** density gradient ultracentrifugation 52
- DOC** sodium deoxycholate xv, 65–70, 159
- DOS** density of states xiv, 39, 45, 46
- DX** dextran 67, 69, 159
- EEA** exciton-exciton annihilation 3, 116, 124, 125
- EL** electroluminescence 54, 56

FCCVD floating catalyst chemical vapor deposition 82

FF far-field 109, 110

FP Fabry–Pérot xiv, xv, 3, 4, 21, 22, 30, 53–60, 97, 100

FWHM full width half maximum 78

IPA isopropyl alcohol 85

IR infrared 26, 27

LB Langmuir–Blodgett 82

LP lower polariton 10, 14–20, 112–115

MCE mixed cellulose ester 84

MQW mili-Q water 159

MWCNT multi-walled carbon nanotube 2, 34, 36–39, 63

NF near-field 109, 110

NIR near infrared 2–4, 28–31, 33, 60, 79, 93, 95, 97, 108–110, 122, 123

NMP N-Methyl-2-Pyrrolidone 84, 85

NPBS non-polarizing beam splitter 110

PC polycarbonate 84

PECVD plasma enhanced chemical vapour deposition 95, 98, 100, 101, 104, 105

PEG polyethylene glycol 67, 69, 159

PFO poly(9,9-di-n-octylfluorenyl-2,7-diyl) 53, 60, 70

PFO-BPy Poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-(6,6'-[2,2'-bipyridine])] xv, xvi, 55, 56, 58–60, 66, 70–78, 80, 83–88, 90, 103, 104, 123

PL photoluminescence xiii, xiv, xvi–xviii, xx, 3, 4, 16, 18, 50–60, 63–65, 81, 83, 84, 87–93, 98, 101, 108–110, 112–121, 123, 124

PLQY photoluminescence quantum yield 52, 53

Q-factor quality factor xvii, 4, 14, 19, 22–27, 54, 55, 57–61, 98, 99, 101, 104–106, 112–114, 116, 117, 121, 123

SC sodium cholate 52, 65, 159

SDS sodium dodecyl sulfate xv, 52, 54, 65–70, 159

SWCNT single-walled carbon nanotube xiii–xvi, xviii, xx, 2–4, 24, 30, 31, 34, 36–39, 44–72, 74–92, 97, 98, 101–109, 111–113, 115, 116, 118, 120–125, 158

TEM transmission electron microscopy 2

TGA thermogravimetric analysis xvi, 77, 80

TMDC transition metal dichalcogenide 27, 29, 30

UP upper polariton 14–17, 20, 112–114

UV ultraviolet 26–30

Vis visible 28–30

VRS vacuum Rabi splitting 15, 16, 56, 57, 59, 112, 113, 115

WGM whispering gallery mode xv, 22, 53, 57, 59, 60

Chapter 1

Introduction

Driven by growing demands for intense and coherent radiation sources across diverse fields over the past five decades, *coherent light*, spanning a broad range of the electromagnetic spectrum, has emerged as a fundamental tool. The advancement of coherent light sources has profoundly revolutionized numerous domains, ranging from high-speed telecommunications and precision materials processing to advanced medical imaging, spectroscopy, metrology, and emerging quantum technologies. Among coherent sources, lasers have become indispensable due to their high brightness, excellent directionality, monochromaticity, and both spatial and temporal coherence. Traditional laser systems, particularly those based on semiconductor materials, have seen widespread application thanks to their electrical compatibility, compact form factor, and tunability. Nonetheless, the quest for laser media with enhanced performance or novel functionalities has spurred significant research interest in nanostructured materials, which offer unique optical properties and opportunities for innovation.

The theoretical foundation for coherent light generation was laid in the early 20th century with Albert Einstein's seminal 1917 introduction of the original concept of *stimulated emission* a process fundamentally rooted in quantum mechanics [57]. In this groundbreaking theory, Einstein described the fundamental process of stimulated emission, which later became the core mechanism underlying laser operation. In this process, an excited atom or molecule, upon interaction with an incident photon of matching energy, is induced to emit a second photon that is identical in energy, phase, and direction to the incident photon. About 30 years later, in 1954, the first MASER (Microwave Amplification by Stimulated Emission of Radiation) was demonstrated by Charles Townes and colleagues, operating in the microwave region [79]. Building upon this breakthrough, the optical analog, the LASER (Light Amplification by Stimulated

Emission of Radiation), was realized in 1960 when Theodore Maiman successfully demonstrated the first ruby laser [147]. This achievement marked the birth of optical coherent light sources.

Throughout the 1960s and 1970s, spanning the next two decades, various types of lasers were developed, including gas lasers (e.g., He-Ne), dye lasers, and semiconductor diode lasers. The 1980s witnessed the rise of solid-state and fiber lasers, which offered improved power, stability, and beam quality. The 1990s and 2000s ushered in the era of ultrafast lasers and frequency comb technologies, further broadening the scope and applications of coherent light [184]. More recently, the focus has expanded to include quantum light sources and coherent emission mechanisms in low-dimensional materials. The discovery of polariton lasing in inorganic semiconductor microcavities in 2003 introduced a fundamentally new route to coherence, through bosonic stimulation and condensation, instead of the traditional population inversion and stimulated emission [49]. These developments have led to the exploration of new materials, including carbon-based nanostructures such as SWCNTs, as potential candidates for next-generation coherent light emitters.

SWCNTs, as quintessential one-dimensional (1D) nanomaterials, exhibit unique optical and electronic properties derived from quantum confinement and chirality-dependent band structures. These characteristics make them strong contenders for miniaturized optoelectronic devices and next-generation light sources. Notably, semiconducting SWCNTs possess direct bandgaps and strong excitonic resonances, supporting efficient light emission in the near infrared (NIR) regime even at room temperature. The origins of carbon nanotube (CNT) research can be traced back to 1889, although the initial observations were limited by insufficient imaging resolution, rendering the nature of the structures unclear. With the advent of transmission electron microscopy (TEM), Russian scientists reported the existence of carbon filaments with a tubular morphology in 1952 [159]. However, these early findings remained largely unrecognized by the broader scientific community. It was not until 1991, when Sumio Iijima utilized high-resolution TEM to clearly identify and characterize multi-walled carbon nanotube (MWCNT)s [100], that CNT research gained significant attention. This landmark discovery marked the beginning of an era of intensive investigation into nanostructured carbon materials. Shortly thereafter, in 1993, Iijima and Donald Bethune independently discovered SWCNTs, marking a pivotal moment in nanoscience [101]. Unlike their multi-walled counterparts, SWCNTs consist of a single graphene sheet rolled into a seamless cylindrical structure with diameters typically ranging from 0.7 to 2 nm. SWCNTs have rapidly garnered attention for their remarkable physical properties. Depending on their chirality, defined by a pair of indices (n, m) that describe the rolling vector of a 2D graphene

sheet into a cylindrical structure, [SWCNTs](#) can exhibit either metallic or semiconducting behavior. Their direct bandgap and strong excitonic effects make semiconducting [SWCNTs](#) particularly attractive for optoelectronic applications.

Over the past three decades, significant advances have been made in the synthesis, purification, and sorting of [SWCNTs](#). Techniques such as arc-discharge, laser ablation, and [chemical vapor deposition \(CVD\)](#) have been developed to produce high-quality nanotubes. Moreover, chirality-selective sorting methods, including density gradient ultracentrifugation, [ATPE](#), and polymer sorting, have enabled researchers to isolate [SWCNTs](#) with specific optical properties. In parallel, studies have shown that [SWCNTs](#) exhibit strong [PL](#) in the [NIR](#) region, long exciton lifetimes, and robust nonlinear optical responses. These features make them excellent candidates for applications in bio-imaging, quantum photonics, and coherent light generation.

Despite these promising features, achieving coherent light emission from [SWCNTs](#) remains a significant challenge due to intrinsic and extrinsic loss mechanisms, such as [PL](#) quenching, [exciton-exciton annihilation \(EEA\)](#), non-radiative recombination, and bundling-induced inhomogeneities continue to pose obstacles to practical device integration. To address these limitations, this work systematically explores the integration of [SWCNTs](#) into high-quality [FP](#) planar microcavities, focusing on the tailored development of gain media, cavity mirrors, and integration strategies. These cavities confine photons in a small spatial volume, enhancing light-matter interactions and enabling access to both weak and strong coupling regimes. The *overarching aim* of this research is to investigate the feasibility of lasing from [SWCNTs](#) in planar cavity geometries, to understand the interplay between cavity design and exciton dynamics, and to lay the groundwork for future quantum nanophotonic systems.

This thesis presents an experimental investigation of light-matter interactions involving [SWCNTs](#), focusing on both the strong-coupling and weak-coupling regimes. The work is organized as follows:

Chapter 2 provides a theoretical overview of photon and polariton lasers, establishing the fundamental principles of light-matter interaction that underpin this study. This chapter also introduces key concepts relevant to coherent light generation in optical cavities.

Chapter 3 offers background information on [SWCNTs](#), highlighting their unique optical properties, excitonic behavior, and potential as a nanoscale gain medium for lasing applications.

Building on these theoretical foundations, Chapter 4 reviews prior research on planar microcavity systems incorporating [SWCNTs](#). Particular attention is given to pre-

vious demonstrations of exciton–polariton formation and photon lasing, which collectively inform the motivation and context for the present work.

Chapter 5 describes the preparation of SWCNT dispersions using ATPE and polymer wrapping sorting methods and compares their characteristics, followed by the fabrication of SWCNT films and characterization of their PL properties. Challenges associated with SWCNT quenching and PL degradation are also discussed in detail.

Chapter 6 details the development of planar microcavities using both Au and DBR mirrors. It comparatively analyzes mirror materials and designs FP cavities for SWCNT films, focusing on their NIR emissions. This chapter also addresses the impact of surface roughness on the microcavity’s Q-factor, outlining fabrication processes for mirrors and planar microcavities.

Chapter 7 carries the optical measurement results obtained from planar microcavity samples. Building on the fabrication of SWCNT thin films and microcavities discussed in previous chapters, this chapter details the optical spectroscopy setups used to characterize SWCNT and microcavity systems, including absorption and PL spectroscopy. It further explores exciton-polariton studies in planar microcavities by comparing different mirror configurations (Au-Au, DBR-Au, and DBR-DBR) and successfully demonstrates photon lasing in SWCNT film.

Finally, Chapter 8 concludes the thesis with a summary of key results and discusses potential directions for future research in the development of nanoscale coherent light sources using SWCNTs.

Chapter 2

Background

2.1 Coherent Light

‘Light’ is an electromagnetic wave characterized by several degrees of freedom such as wavelength (frequency), amplitude, phase, and polarization (which is related to angular momentum such as right- or left-handed circular polarization). ‘Coherent light’ refers to the light with a fixed phase, exhibiting both temporal and spatial coherence. Suppose an arc lamp emits the incoherent light comprising multiple wavelengths with a random phase relationship. When the light propagates through a pinhole aperture, which serves as a spatial filter, its spatial coherence is improved. Subsequently, passing through a wavelength-selective filter acting as a spectral filter enhances its temporal coherence (Fig. 2.1(a)). This situation can be better understood by plotting the wavefunctions in the time domain. Figure 2.1(b)-(d) illustrates three cases: incoherent light consisting of many out-of-phase wavelengths (b), incoherent but monochromatic light (c), and coherent light (d), respectively.

Temporal coherence means how well the phase of a light wave is sustained over time at a given point in space. The coherent light in Fig. 2.1(d) is a good example of the temporal coherence wave function, and the light with a narrow spectral linewidth has high temporal coherence. The definition of spatial coherence is how well the phase of a light wave is correlated across different points in space, namely, how uniformly the wavefront propagates across a distance. Temporal coherence is observed from a time-delayed overlapped pattern using a Michelson interferometer, while spatial coherence is measured by a modified Michelson interferometer, which overlap two images, one from the original beam path and the other from a flipped path, as illustrated in Fig. 2.1(e) and

(f). Those two images display high-contrast interference fringes, demonstrating that the light is spatially coherent.

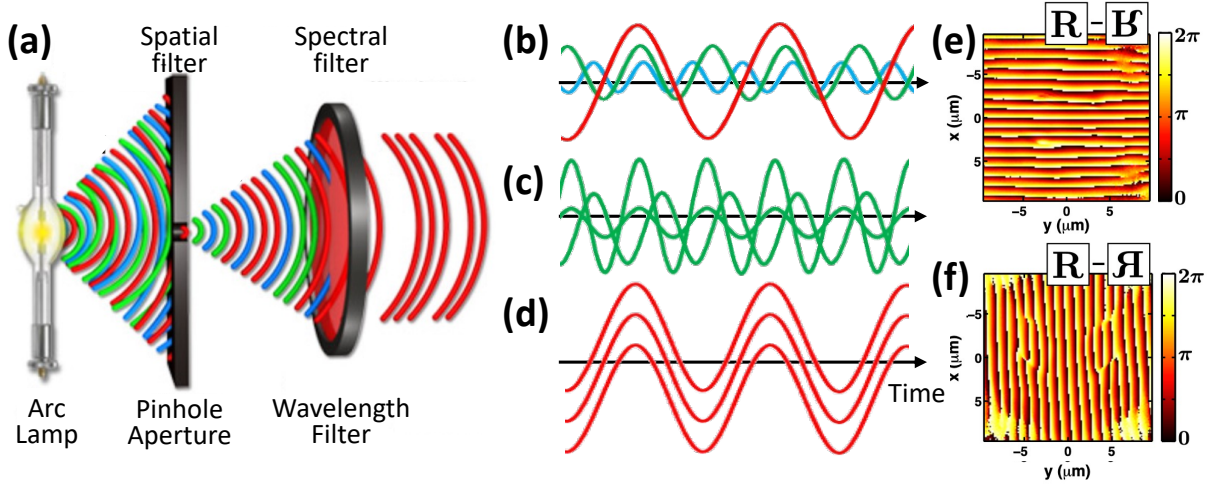


Figure 2.1: (a) Schematics for the process from incoherent light to coherent light by a pinhole and filter reproduced and revised from [7]. Light propagation in the time domain for (b) multi-wavelength incoherent light, (c) monochromatic incoherent light, and (d) monochromatic coherent light, which is the temporal coherent. Spatial coherence is directly measured by overlapping a flipped image along the vertical (e) or the horizontal (f) orientations with the original one adapted from [178].

Coherent light sources are widely used in various areas, including precision metrology and high-resolution imaging, high-speed communication, military and defense, as well as quantum computing and cryptography. Such coherent light sources are photon lasers, polariton lasers, synchrotron radiation sources, and free-electron lasers [197]. Photon lasers are the most common and conventional type of coherent light sources encountered in everyday life. Since the first working laser based on ruby crystals in 1960 [147], they are ubiquitous in devices such as laser pointers, barcode scanners, CD/DVD/Blu-ray players, and various medical instruments. Additionally, photon lasers play a significant role in various scientific and technological applications, including fiber-optic communication, industrial processing, and military equipment. As a coherent light source rooted from fundamentally different principles from conventional photon lasers, polariton-lasers, first demonstrated in 2003 [49], are a relatively recent development. Although not yet commercially available, they have been actively studied due to their advantage, a remarkably lower threshold to generate coherent light in comparison to photon lasers, making them highly energy efficient.

Synchrotron radiation is the electromagnetic radiation generated through the acceleration of relativistic electrons along curved paths by changing the direction with magnetic fields. This method makes a broadband spectrum range from infrared to X-rays with high spatial coherence, though it typically exhibits low temporal coherence. On the other hand, free-electron lasers use the same high-speed electrons, but their emission comes from a different mechanism. Electrons travel in a straight line through an undulator, an array of alternating magnetic fields, which induces transverse oscillations. These oscillations lead to collective electron interactions and micro-bunching, resulting in the emission of light that is both spatially and temporally coherent [197].

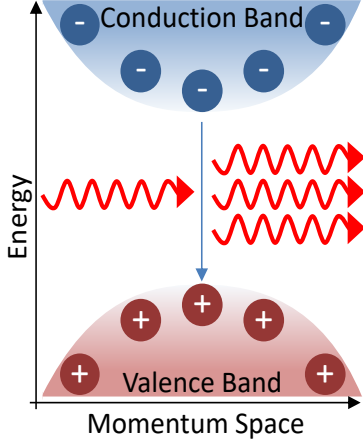
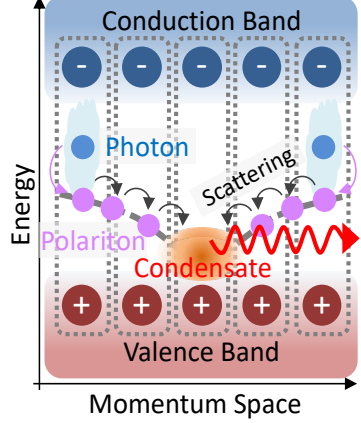
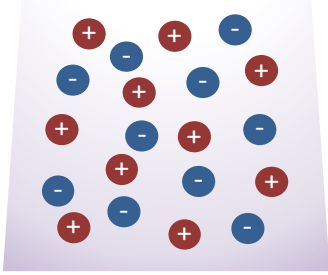
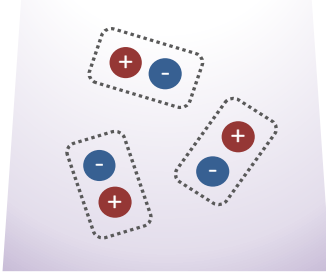
Among those coherent light sources, photon lasers can be broadly classified based on the nature of their gain medium, including solid-state, gas, dye, and semiconductor lasers. Solid-state lasers, such as the Nd:YAG (neodymium-doped yttrium aluminum garnet) laser, employ a crystalline or glass host material doped with rare-earth or transition metal ions. These lasers are recognized for their high output power, excellent beam quality, and relatively high efficiency. Gas lasers, including He-Ne and CO₂ lasers, use a gaseous medium excited by electrical discharge. He-Ne lasers are valued for their stable output and narrow linewidths, while CO₂ lasers are particularly effective in high-power infrared applications. Dye lasers utilize organic dye molecules dissolved in solvents as the gain medium, enabling broad wavelength tunability. Although they require complex operation and frequent maintenance, dye lasers are indispensable in applications demanding precise wavelength control. Semiconductor lasers, or laser diodes, generate coherent light through electron-hole recombination within semiconductor junctions. Their compact size, electrical efficiency, and integrability make them essential in a wide range of photonic technologies [197].

Of the various coherent light sources, photon laser, specifically semiconductor lasers and polariton lasers are of particular interest due to their closer relevance to everyday and industrial applications, cost-effectiveness, and strong potential as candidates for future quantum devices.

2.2 Photon Lasers and Polariton Lasers

Both photon lasers and polariton lasers produce coherent light; however, they operate through fundamentally distinct physical mechanisms. Photon lasers rely on the principle of stimulated emission within a population-inverted gain medium, whereas polariton lasers achieve coherence from a bosonic stimulated scattering process bypassing the need for population inversion. Table 2.1 summarizes the key differences be-

Table 2.1: Comparison between photon and polariton lasers. Schematic illustrations in the top row are adapted and modified from [29], and those in the fourth row from the bottom are adapted and modified from [96].

	Photon Laser	Polariton Laser
Principle		
Electron & Hole Distribution	strong inversion	no inversion
Characteristic Length	a_B (nm scale)	λ_t (μm scale)
Carrier Density	$n \gg n_{\text{Mott}}$	$n \ll n_{\text{Mott}}$
In Real Space		
Gain Type	fermionic	bosonic
Constituent quasi-particle	$e-h$ plasma, unbound	exciton-polariton with bound exciton
Emission Energy	near cavity mode	below cavity mode

tween two coherent light sources in terms of operation principle, carrier distribution, carrier density, gain type, emission energy, etc.

The concept of stimulated emission, first predicted by Albert Einstein in 1917 [57], describes a process in which a group of excited electrons, when stimulated by incoming photons identical to themselves, coherently emit additional photons with the same phase, frequency, and direction. The term “LASER,” an acronym for “Light Amplification by Stimulated Emission of Radiation,” was coined by Gordon Gould in 1957, forty years after Einstein’s prediction. It has since become a common noun due to its widespread use in everyday life. A prerequisite for stimulated emission is **population inversion**, a condition in which more electrons occupy excited states (e.g. the conduction band) than the ground state (e.g. the valence band). This inversion is essential for ensuring that stimulated emission outweighs absorption, a critical requirement for laser operation.

The behavior of light within a laser medium is governed by the interplay between gain and loss. **Gain** refers to the amplification of light intensity as it propagates through the medium, primarily driven by stimulated emission from excited electrons. In contrast, **loss** encompasses mechanisms that reduce light intensity, such as absorption, scattering, imperfections in optical components, and insufficient mirror reflectivity at the boundaries of the gain medium. When the optical gain exceeds the total losses in the system, net amplification occurs, allowing the onset of lasing. Conversely, if the losses outweigh the gain, sustained laser oscillations cannot be achieved. Therefore, population inversion within the gain medium enables stimulated emission to surpass absorption, resulting in net optical gain.

When this gain exceeds the intrinsic losses of both the medium and the optical cavity, continuous laser oscillations become possible. Under strong population inversion, the carrier density significantly exceeds the Mott density, which is a critical carrier threshold density beyond which excitons are dissociated due to many-body screening effects. At this point, the material undergoes a transition from an insulating excitonic state to a conducting electron–hole plasma phase. Specifically, when the density of photoexcited electron–hole pairs surpasses the Mott density (n_{Mott}), the Coulomb interaction between electrons and holes is sufficiently screened, leading to the breakdown of bound excitons and the formation of a free carrier plasma. In three-dimensional bulk systems, the Mott density is approximately inversely proportional to the cube of the exciton Bohr radius (a_{B}), expressed as $n_{\text{Mott}} \sim \left(\frac{1}{a_{\text{B}}^3}\right)$. Therefore, the quasi-particles in the real space are illustrated by electron-hole pairs as shown in Table 2.1. In photon lasers, the active medium consists of an unbound electron–hole plasma, exhibiting fermionic

characteristics. The emission energy typically occurs near the cavity mode.

On the other hand, polariton lasers operate based on the Bose-Einstein condensation of exciton–polaritons, quasiparticles resulting from the strong coupling between cavity photons and excitons, which are Coulombically bound electron–hole pairs in a semiconductor microcavity. Unlike conventional photon lasers, polariton lasers achieve macroscopic coherence via bosonic final-state stimulation, without requiring full inversion of electronic populations. The condensation arises from the stimulated scattering of exciton–polaritons or polariton–polariton interaction into the lowest-energy state. This process is accompanied by stimulated cooling, enabled by the bosonic nature of polaritons. When the density of polaritons reaches a critical threshold, exciton–polaritons spontaneously accumulate in the lowest-energy state (typically at zero in-plane momentum), resulting in coherent light emission. This process occurs below the Mott density, where excitons remain stable and bound. The critical density threshold for polariton condensation is associated with the thermal de Broglie wavelength, λ_t , which characterizes the spatial extent of a polariton wavefunction. Condensation occurs when the interparticle distance becomes comparable to λ_t , which is typically an order of magnitude larger than a_B . As a result, the critical density required for polariton laser is significantly lower (typically two orders of magnitude lower) than that for conventional polariton lasing.

Carriers, optically or electrically injected in the linear regime at densities below the Mott threshold, form excitons that strongly couple with cavity photons. As a manifestation of the strong coupling between exciton and photons, two distinct branches, upper and lower exciton–polaritons, emerge. Keeping the carrier density low to moderate prevents the formation of a free electron–hole plasma, which would destroy the excitonic resonance required for strong coupling. Consequently, population inversion is not required, distinguishing polariton lasers from photon lasers. As the density of exciton–polaritons approaches the quantum degeneracy threshold, their momentum distribution narrows, signaling the onset of exciton–polariton lasing. In real space, the polariton condensate extends macroscopically while remaining confined to a single spatial mode [49], and its spatial distribution can be engineered by the excitation profile [178], in-plane trap potentials [119], or intrinsic disorder [126].

Exciton–polaritons are hybrid quantum quasiparticles with dual part-light (photon) and part-matter (exciton) characteristics. Their light mass and strong nonlinear interactions make them ideal candidates for achieving condensation at relatively high temperatures and low density thresholds. The emission energy of a polariton laser corresponds to the bottom of the [lower polariton \(LP\)](#) branch, which lies below the bare cavity photon mode due to strong coupling. The exact emission energy depends on the detuning between the cavity photon mode and the exciton resonance, as well as

the exciton-photon coupling strength. In contrast to photon lasers with engineered photonic band gaps for spectral control, the spectral properties of polariton lasers are governed by the polaritonic dispersion relation.

The next section will further explore the photon laser and polariton laser in the context of light-matter interaction.

2.3 Light-Matter Interaction

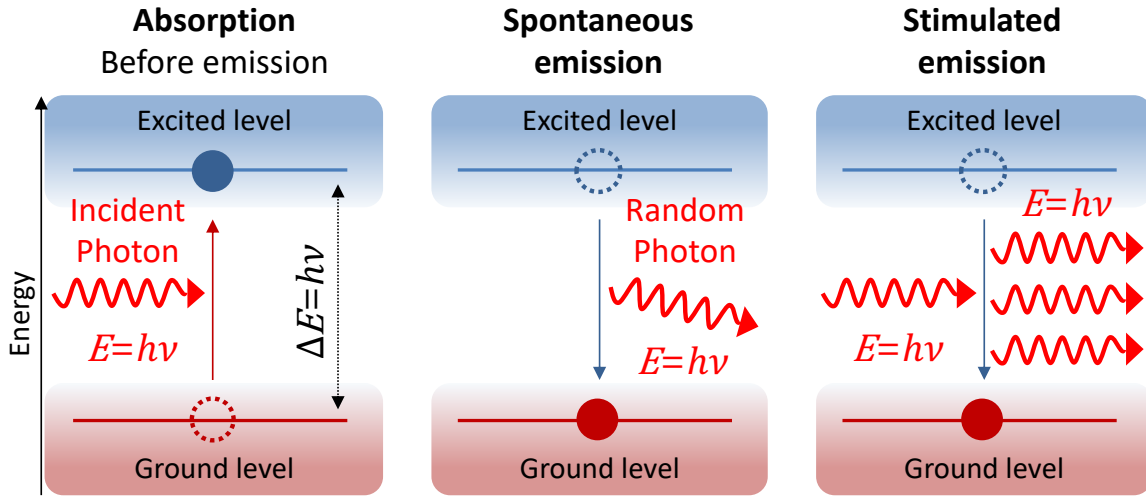


Figure 2.2: Fundamental processes governing the interaction of electromagnetic radiation with matter: absorption, spontaneous emission, and stimulated emission.

At the core of many optical phenomena lies the principle of light-matter interaction. Understanding how light interacts with matter is fundamental to the design and function of optical devices, including light-emitting diodes, photodetectors, lasers, and quantum emitters. When light interacts with a material system such as atoms, molecules, or semiconductors, three primary processes can occur: absorption, spontaneous, and stimulated emission (Fig. 2.2). In **absorption**, the photon energy is transferred to promote an electron in the material to a higher energy state. Conversely, **spontaneous emission** occurs when an excited electron naturally decays to a lower energy state, releasing a photon without any external influence. **Stimulated emission** takes

place when an incoming photon induces an excited electron to drop to a lower energy level, emitting a second photon that is coherent with the first. These three mechanisms are central to the operation of both photon and polariton lasers, as they govern how light is generated, manipulated, and amplified within a medium.

In particular, to amplify light in a photon laser or to generate polaritons in a polariton laser, photons must be confined within a defined spatial region containing matter. This confinement is typically engineered using photonic structures such as optical cavities, DBRs, which trap photons and enhance their interaction with the material. Under such conditions, interaction between light and matter becomes inevitable and often pronounced, enabling key processes like stimulated emission in photon lasers or strong coupling in polariton lasers. This section discusses the operational principles of photon and polariton lasers in the context of light-matter interaction.

Suppose a sufficient number of photons exist within a gain medium confined along the z -axis, effectively forming a 2D plane. In this configuration (Fig. 2.3(a)), the photonic degrees of freedom are quantized along the z -axis (fixed, $k_{\perp}$), while they remain free in the transverse xy -plane ($k_{\parallel}$). The confined photons interact with the gain medium, leading to the generation of excitons in semiconductors, which can subsequently interact with the photons. Figure 2.3(b) presents a schematic illustration of this light-matter interaction: light, represented as a photon wave, and matter, represented as an exciton, a quasiparticle formed by the binding of an electron and a hole. In the absence of light-matter coupling, or under weak coupling conditions, the system consists of cavity photons ($E_{\text{cav}}(k_{\parallel})$) that behave as bosons and exhibit a parabolic energy dispersion with respect to the in-plane momentum $k_{\parallel}$, corresponding to the xy -plane:

$$\begin{aligned}
 E_{\text{cav}}(k_{\parallel}) &= \frac{\hbar c}{n_c} \sqrt{(k_{\perp}^2 + k_{\parallel}^2)}, \\
 &= \frac{\hbar c}{n_c} k_{\perp} \left(1 + \left(\frac{k_{\parallel}}{k_{\perp}} \right)^2 \right)^{\frac{1}{2}}, \\
 &\simeq \frac{\hbar c}{n_c} k_{\perp} \left(1 + \frac{k_{\parallel}^2}{2k_{\perp}^2} \right) \quad (\text{when, } k_{\parallel} \ll k_{\perp}), \\
 &= E_{\text{cav}}(k_{\parallel} = 0) + \frac{\hbar^2}{2m^*} k_{\parallel}^2.
 \end{aligned} \tag{2.1}$$

Here, $\hbar$ is the reduced Planck constant, c is the speed of light, n_c is the refractive index of the cavity, $k_{\perp}$ denotes the momentum component along the longitudinal z -direction, and m^* is the effective mass of the photon within the cavity arising from the broken

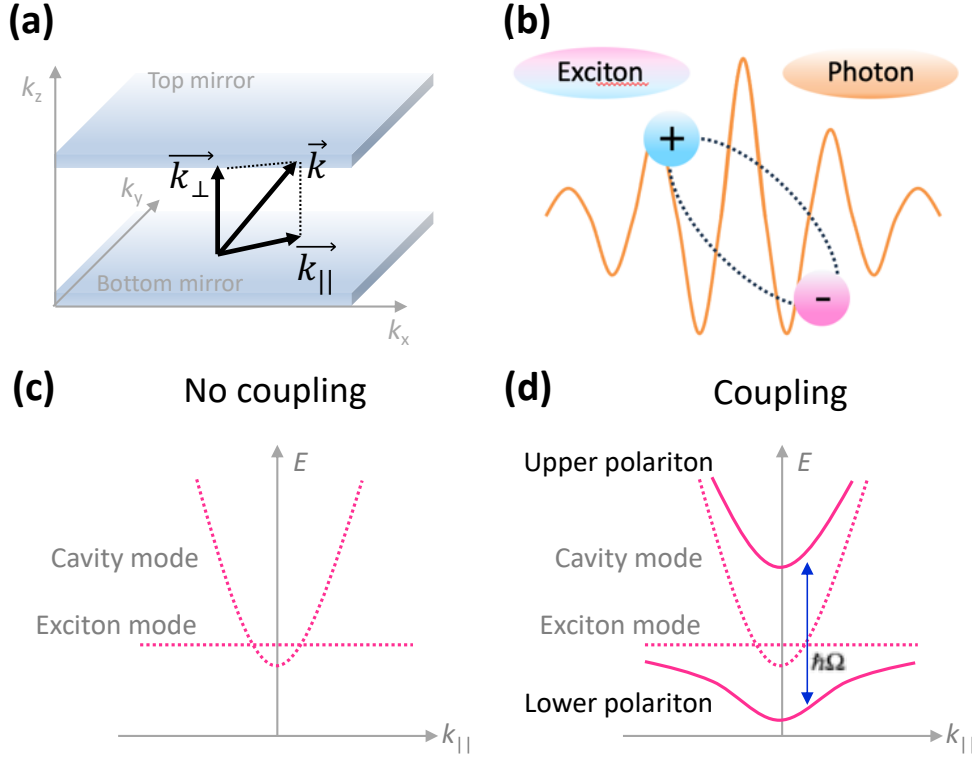


Figure 2.3: (a) Incident light in a planar microcavity and its wavevector $\vec{k}$, which is decomposed into components perpendicular ($\vec{k}_\perp$) and parallel ($\vec{k}_\parallel$) to the mirror plane. (b) A schematic illustration of the interaction between light (photons, represented as waves) and matter (excitons, composed of an electron and a hole). (c) Energy dispersions in $2D$ momentum $k_\parallel$ space in the absence of coupling, and (d) energy dispersions of upper and lower polaritons under coupling in $2D$ space confined along the growth direction. $\hbar\Omega$ is the strength of the exciton-photon coupling.

translational invariance along the z -axis. Interestingly, photons, which are massless in a vacuum, acquire an effective mass when confined in the microcavity whose $k_\perp$ is much bigger than $k_\parallel$. This effective mass is given by $m^* = \frac{2\pi\hbar}{\lambda_c c}$, where λ_c is the cavity resonance wavelength. Typically, the photon effective mass lies in the range of $10^{-5} - 10^{-4} m_e$, where m_e is the free electron mass.

Excitons, which are bosonic quasiparticles composed of bound electron-hole pairs (composite fermions), exhibit a flat or nearly flat dispersion in comparison to the cav-

ity photon mode. This is because the effective mass of excitons is typically more than three orders of magnitude larger than that of cavity photons. As a result, when both dispersions are plotted in the same momentum space, the exciton dispersion appears flat, almost constant, compared to the parabolic dispersion of the cavity photon mode in Fig. 2.3(c).

The Hamiltonian of the exciton–photon system, in the absence of coupling, includes decay (or dissipation) terms represented by imaginary components: $i\hbar\frac{\gamma_c}{2}$ and $i\hbar\frac{\gamma_x}{2}$. These terms account for losses due to imperfections in the device and the finite lifetimes of the cavity and exciton states. The parameter γ_x represents the broadening arising from exciton interactions, such as interparticle scattering and exciton–phonon coupling. In contrast, γ_c corresponds to cavity photon losses, primarily determined by the finite reflectivity of the mirrors, and is inversely proportional to the cavity’s **Q-factor**. Both γ values are inversely related to the lifetimes of the respective states, with $\tau_c = \gamma_c^{-1}$ and $\tau_x = \gamma_x^{-1}$. With these considerations, the uncoupled Hamiltonian matrix is given by:

$$H_{\text{uncoupled}}(k_{\parallel}) = \begin{pmatrix} E_c(k_{\parallel}) - i\hbar\frac{\gamma_c}{2} & 0 \\ 0 & E_x(k_{\parallel}) - i\hbar\frac{\gamma_x}{2} \end{pmatrix}. \quad (2.2)$$

Since the Hamiltonian is diagonal in the absence of coupling (i.e., coupling terms are zero), the energies of the cavity mode ($E_c(k_{\parallel})$) and the exciton mode ($E_x(k_{\parallel})$) behave independently, each maintaining its characteristics. As a result, their dispersion curves intersect without exhibiting anti-crossing behavior.

In contrast, when coupling is present, the Hamiltonian includes off-diagonal terms, $\frac{\hbar\Omega_R}{2}$, which represent the coupling strength arising from exciton–photon dipole interactions. The light–matter coupling Hamiltonian, incorporating the finite lifetimes of photons and excitons in realistic systems, is given by:

$$H_{\text{coupling}}(k_{\parallel}) = \begin{pmatrix} E_c(k_{\parallel}) - i\hbar\frac{\gamma_c}{2} & \frac{\hbar\Omega_R}{2} \\ \frac{\hbar\Omega_R}{2} & E_x(k_{\parallel}) - i\hbar\frac{\gamma_x}{2} \end{pmatrix}. \quad (2.3)$$

Two eigenstates, corresponding to the energy states of the **upper polariton (UP)** and **LP**, are obtained by diagonalizing the coupling Hamiltonian $H_{\text{coupling}}(k_{\parallel})$, and are given by (Fig. 2.3(d)):

$$E_{\text{LP,UP}}(k_{\parallel}) = \frac{E_c(k_{\parallel}) + E_x(k_{\parallel})}{2} - i\hbar \frac{\gamma_c + \gamma_x}{4} \mp \frac{1}{2} \sqrt{\left(E_c(k_{\parallel}) - E_x(k_{\parallel}) - i\hbar \frac{\gamma_c - \gamma_x}{2}\right)^2 + (\hbar\Omega_R)^2}. \quad (2.4)$$

Depending on the coupling strength, the system falls into either the weak or strong coupling regime:

- **Strong coupling:** $\Omega_R \gg \frac{\gamma_c - \gamma_x}{2}$
- **Weak coupling:** $\Omega_R \ll \frac{\gamma_c - \gamma_x}{2}$.

Weak coupling typically arises under conditions such as a low-quality optical cavity (i.e., a high photon decay rate γ_c), low exciton oscillator strength, and significant detuning between the exciton and cavity modes. Under these circumstances—along with a very small coupling strength Ω_R , the off-diagonal coupling terms in the Hamiltonian are often negligible, and the system can be adequately described by uncoupled energy dispersions. In contrast, **Strong coupling** occurs when Ω_R is sufficiently large such that coherent energy exchange between the exciton and photon modes dominates over the decay rates. This regime is characterized by normal-mode splitting (i.e., anti-crossing behavior) in the dispersion relation, resulting in the appearance of the **vacuum Rabi splitting (VRS)**, denoted by $\hbar\Omega$. Physically, this indicates that the light–matter interaction is strong enough to overcome losses and support the formation of hybridized exciton–photon states.

The difference between $E_c(k_{\parallel})$ and $E_x(k_{\parallel})$ in the square root term of the polariton dispersion relation defines the detuning parameter, Δ , given by:

$$\Delta = E_c(k_{\parallel}) - E_x(k_{\parallel}) \quad (2.5)$$

In the case of negative detuning (red detuning, $\Delta < 0$), the **LP** has a more photonic character, whereas in positive detuning (blue detuning, $\Delta > 0$), the **UP** exhibits a more excitonic nature.

A polariton is a coherent superposition of an exciton and a photon with the same in-plane wavevector $k_{\parallel}$. Since both excitons and photons are bosons, polaritons also obey bosonic statistics. The relative contributions of the exciton and photon to the polariton states are quantified by the squared amplitudes of $X_{k_{\parallel}}$ and $C_{k_{\parallel}}$, known as the Hopfield coefficients [93].

The Hopfield coefficients satisfy the normalization condition:

$$|X_{k_{\parallel}}|^2 + |C_{k_{\parallel}}|^2 = 1. \quad (2.6)$$

As a function of detuning Δ and **VRS** $\hbar\Omega$, they are expressed as:

$$\begin{aligned} |X_{k_{\parallel}}|^2 &= \frac{1}{2} \left(1 + \frac{\Delta}{\sqrt{\Delta^2 + \hbar^2 \Omega^2}} \right) \\ |C_{k_{\parallel}}|^2 &= \frac{1}{2} \left(1 - \frac{\Delta}{\sqrt{\Delta^2 + \hbar^2 \Omega^2}} \right) \end{aligned} \quad (2.7)$$

At zero detuning ($\Delta = 0$), the Hopfield coefficients become equal: $|X_{k_{\parallel}}|^2 = |C_{k_{\parallel}}|^2 = \frac{1}{2}$, indicating that both the **LP** and **UP** states are composed of an equal mixture of exciton and photon.

The three detuning regimes, positive, zero, and negative, affect the exciton and photon fractions in the polariton states. These variations are illustrated in Fig. 2.4, where the Hopfield coefficients and corresponding **LP** and **UP** energy branches are plotted [48].

The real part of Eq. 2.4 corresponds to the observable polariton dispersion in the **PL** spectra, labeled as $E_{\text{LP}}(k_{\parallel})$ for the **LP** and $E_{\text{UP}}(k_{\parallel})$ for the **UP**. These polariton branches arise from the hybridization of the cavity photon mode and the exciton mode and exhibit an energy splitting at the anti-crossing point in momentum space. The energy separation between the two polariton branches at zero detuning (i.e., at the anti-crossing point) is referred to as the **VRS**, denoted by $\hbar\Omega_R$, which quantifies the strength of the light-matter coupling.

The imaginary part of Eq. 2.4 represents the decay rate of the polaritons. This decay is primarily governed by photon leakage, characterized by the photon decay rate γ_c , as cavity photons can rapidly escape the structure. In typical III-V semiconductor microcavities (e.g., GaAs-based systems), the photon lifetime is on the order of 1–10 ps, depending on the quality factor Q of the cavity. The quality factor is related to the photon decay rate by:

$$Q = \frac{E_c}{\hbar\gamma_c}. \quad (2.8)$$

The exciton decay rate γ_x is generally slower, on the order of 100 ps, but still contributes to the total polariton linewidth. The polariton decay rates (linewidths) for the

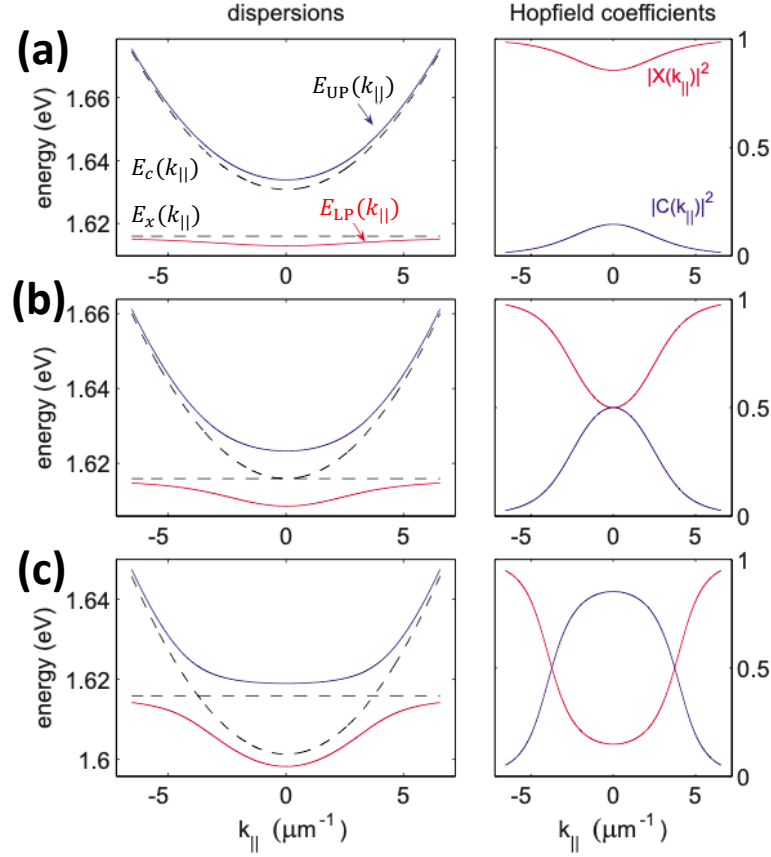


Figure 2.4: Polariton dispersions and corresponding Hopfield coefficients at (a) positive detuning, (b) zero detuning, (c) negative detuning adapted from[48].

LP and UP are given as weighted sums of the exciton and photon decay rates, with weights defined by the Hopfield coefficients:

$$\begin{aligned}\gamma_{\text{LP}} &= |X_{k_{\parallel}}|^2 \gamma_x + |C_{k_{\parallel}}|^2 \gamma_c, \\ \gamma_{\text{UP}} &= |C_{k_{\parallel}}|^2 \gamma_x + |X_{k_{\parallel}}|^2 \gamma_c.\end{aligned}\tag{2.9}$$

These expressions reflect the hybrid nature of polaritons, whose linewidths are influenced by both excitonic and photonic decay channels.

After polaritons are created through strong light–matter interactions, an additional step, stimulated scattering by polariton particle density control with the excitation laser

intensity, is required for condensation to occur. Due to their short lifetimes, typically on the order of picoseconds, the polariton system operates as a driven-dissipative, non-equilibrium system. Excitons are continuously injected either optically (via a pump laser) or electrically (through a voltage bias), creating polaritons that subsequently decay by emitting light. The system reaches a steady state when the input (pumping) balances the losses. At sufficiently high polariton densities, though still below the Mott transition threshold, stimulated scattering drives polaritons into the lowest energy state at $k_{\parallel} \approx 0$. Owing to their bosonic nature, polaritons preferentially accumulate in this state, such that $n(k_{\parallel} = 0) \gg n(k_{\parallel} \neq 0)$. This macroscopic occupation of a single quantum state is analogous to Bose–Einstein condensation, albeit occurring under non-equilibrium conditions (Fig. 2.5(a)).

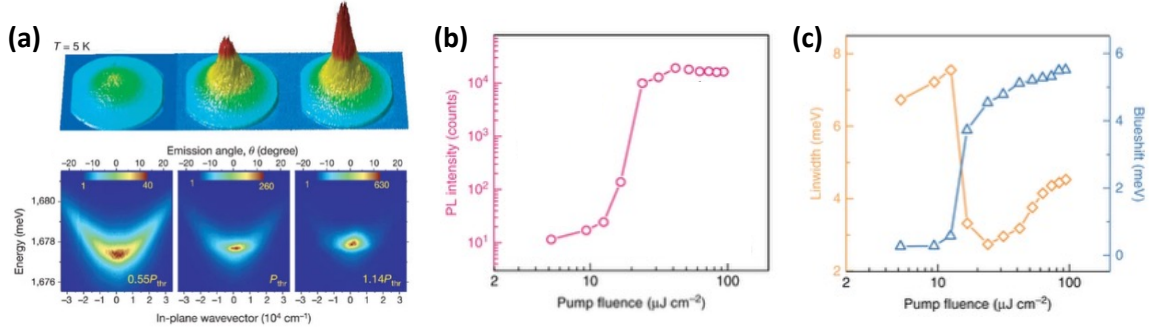


Figure 2.5: Exciton-polariton condensation behavior under varying pump power. (a) Exciton-polariton emission shown in both 3D (upper) and 2D PL data, spanning from below to above the condensation threshold, demonstrating the formation of a polariton condensate adapted from [114]. (b) Pump power dependence of PL intensity at $k_{\parallel} = 0$, revealing the nonlinear response characteristic of polariton condensation reprinted from [220]. (c) Corresponding pump power dependence of the spectral linewidth and peak emission energy at $k_{\parallel} = 0$ reproduced from [220].

The signatures of polariton condensation include macroscopic occupation of a single quantum state (Fig. 2.5(a) [114]), threshold behavior (Fig. 2.5(b) [220]), long-range spatial coherence, spectral narrowing of the emission, and blueshift (Fig. 2.5(c) [220]) as a function of pump power. Especially, threshold pump power is typically lower than that of conventional photon lasers. Additional evidence, such as the formation of quantized vortices or spontaneous symmetry breaking, can also indicate the presence of a condensate. Among these phenomena, polariton lasing arises from the macroscopic occupation of the LP mode. The emitted light is coherent and directional, resembling conventional laser emission. Although polariton lasing originates from the lowest energy state in the

LP branch, a blueshift is often observed in the condensate due to polariton–polariton interactions and increased density.

Table 2.2: Comparison of Coupling Regimes in Photon and Polariton Lasers.

	Photon Laser	Polariton Laser
Coupling Regime	Weak coupling	Strong coupling
Light-Matter Interaction	Light stimulates coherent emission from unbound electron-hole plasma	Coherent exchange between cavity photons and bound excitons
Key Mechanism	Stimulated emission of photons	Bose-Einstein condensation of polaritons
Carrier Distribution	High-density, thermalized carriers (holes and electrons)	Non-equilibrium bosonic population of polaritons
Gain Mechanism	Optical gain from stimulated recombination of carriers	Bosonic stimulation into the ground polariton state
Quasi-particles	Photons only (fermionic gain medium)	Exciton-polaritons (bosonic light-matter quasi-particles)
Spectral Characteristics	Narrow, single-mode emission with sharp threshold	Broader, softer threshold

Through a review of photon lasers, polariton lasers, and light–matter interaction systems, the underlying connections among them become evident in Table 2.2. Photon lasers operate in the weak coupling regime of light–matter interaction, whereas polariton lasers arise in the strong coupling regime. In photon lasers, light generation involves two key processes: absorption, where the material absorbs pump energy to excite electrons, and stimulated emission, where incoming photons trigger the recombination of excited electrons and holes, emitting coherent light. This inherently requires interaction between light and matter. Lasing occurs when optical gain exceeds losses, a balance governed by factors such as the cavity Q-factor, mirror reflectivity, and carrier injection, which will be discussed in the next section. Notably, without any light–matter coupling, the cavity field and the gain medium would be completely decoupled, making stimulated emission, and thus lasing, impossible.

Strong coupling is a prerequisite for polariton lasers. In this regime, the system

enables a reversible energy exchange between photons and excitons, resulting in the formation of new eigenstates: the LP and UP branches. Subsequently, through scattering processes, polaritons relax in energy and accumulate at the bottom of the LP branch, eventually forming a polariton condensate. This condensation leads to polariton lasing, which occurs without the need for population inversion.

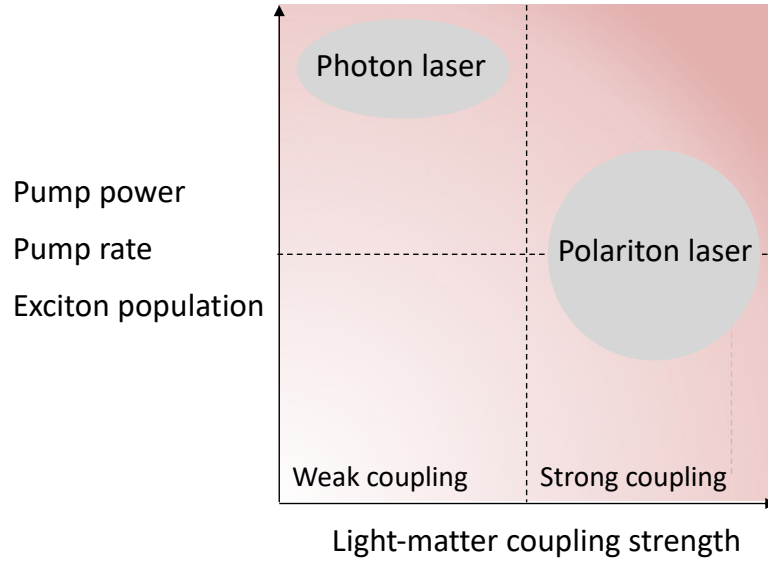


Figure 2.6: A four-block diagram can represent photon and polariton lasers according to the strength of light–matter interaction and external parameters including pump power, pump rate, or exciton density.

Ultimately, photon lasers and polariton lasers can be mapped onto a four-quadrant diagram, with light–matter interaction strength on the x-axis and density, related parameters, such as pump power, pump rate, or exciton population, on the y-axis. As discussed previously, photon laser is the regime of weak coupling and requires high density to make the population inversion, it should be above threshold pump power or above the Mott density [185, 114].

On the other hand, for polariton lasers, strong coupling is essential to generate polaritons in the first place. A certain threshold of pump power is required to initiate scattering processes that lead to polariton condensation. However, if the pump power becomes too high, the system may undergo a Mott transition, where the exciton density exceeds a critical value and excitons dissociate into an electron–hole plasma, thereby screening the Coulomb interaction and destroying the exciton population [48, 185].

This leads to the breakdown of strong coupling and collapse of the polariton condensate. As a result, coherence is lost, and polariton lasing is suppressed [114, 30].

2.4 Microcavity

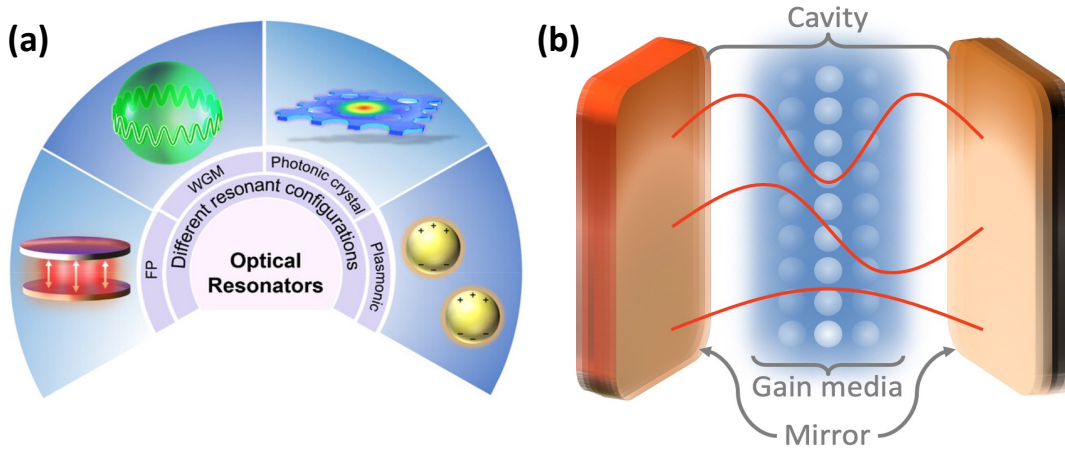


Figure 2.7: (a) Optical resonators include Fabry-Pérot (FP) cavities, whispering gallery modes (WGM), photonic crystals, and plasmonic structures adapted from [233]. (b) An illustration of a Fabry-Pérot cavity showing its internal structure in detail.

Both photon lasers and polariton lasers fundamentally rely on the confinement of photons to enhance light-matter interactions and enable efficient light amplification. This confinement is realized through the use of optical resonators, which play a critical role in controlling the spatial and spectral properties of the electromagnetic field, thereby facilitating processes such as stimulated emission in photon lasers and strong coupling in polariton systems. There are four commonly used resonators in Fig 2.7(a): FP cavities, whispering gallery modes, photonic crystals, and plasmonic structures.

A FP cavity consists of two parallel, highly reflective mirrors separated by a cavity of fixed or tunable length. Light undergoes multiple reflections between the mirrors, and resonance occurs when the round-trip optical path length is an integer multiple of the wavelength, resulting in the formation of standing waves within the cavity [184]. Due to its simple structure and ease of fabrication, the FP cavity is widely employed in a range of optical devices [232]. It offers high finesse, sharp resonance characteristics, and broad tunability [143]. However, in free-space implementations, it is often bulky,

highly sensitive to alignment, and typically limited to specific polarization states [192]. Despite these limitations, FP cavities are extensively utilized in applications such as wavelength filtering, diode lasers, optical sensing, and spectroscopy [27].

Light propagates along the perimeter of circular or toroidal dielectric structures, such as microspheres or microdisks, via total internal reflection, forming standing waves known as WGM resonators. These resonators are characterized by ultra-high Q-factor values and small mode volumes, which enable strong light–matter interactions. They are also compact and suitable for integration into photonic circuits [211]. However, WGM resonators present challenges, including difficult optical coupling and tuning, sensitivity to environmental changes such as temperature and pressure, and complex fabrication processes required to achieve high Q-factor performance. Despite these limitations, they are widely employed in applications such as biosensing, nonlinear optics, and frequency comb generation [120, 214].

Photonic crystal resonators are periodic dielectric structures that create a photonic bandgap, thereby prohibiting the propagation of light at certain wavelengths. By introducing local defects into the periodic structure, light can be confined in nanocavities. These resonators offer ultra-small mode volumes, highly tailorable spectral properties, and excellent compatibility with photonic integrated circuits [109]. However, their fabrication is challenging due to the nanoscale precision required, and they are sensitive to structural disorder and imperfections. Additionally, their operational spectral range is typically limited. Despite these challenges, photonic crystal resonators are widely used in applications such as integrated photonic chips, on-chip lasers, single-photon sources, and slow light devices [9, 166].

Plasmonic resonators exploit surface plasmons, collective oscillations of electrons, excited at metal–dielectric interfaces with sharp tips, grooves, or gaps to enable sub-wavelength confinement of light. These resonators offer ultra-compact footprints beyond the diffraction limit, strong electromagnetic field enhancement, and fast response times [146]. However, they suffer from significant absorption losses, particularly in metals, as well as limited Q-factor and potential thermal management issues. Despite these limitations, plasmonic resonators are widely used in applications such as nanoscale sensing, photothermal therapy, plasmonic nanolasers, and the enhancement of nonlinear optical effects [16, 170].

A summary of these resonators is presented in Table 2.3.

Based on the comparative analysis of different resonator structures, the FP cavity was selected as the most suitable architecture for our device system. A magnified view of the cavity is shown in Fig. 2.7(b). As illustrated, two parallel mirrors are placed on

Table 2.3: Comparison of typical optical resonators.

Resonator Type	Fabry-Pérot cavity	Whispering gallery mode	Photonic Crystal	Plasmonic resonator
Principle	Multiple reflections	Total internal reflection	Photonic bandgap	Surface plasmon resonance
Pros	Simple, high finesse	Ultra-high Q-factor , compact	Small mode volume, integrable	Subwavelength, high field
Cons	Bulky, alignment-sensitive	Coupling difficulty	Fabrication complexity	lossy, low Q-factor
Applications	Lasers, filters, spectroscopy	Biosensing, frequency combs	On-chip lasers	Nanosensors

either side of the structure, confining photons between them to form what is known as an optical cavity. This cavity acts as a resonant defect that selectively supports specific photon modes, determined by the cavity thickness.

The cavity thickness L defines the wavelengths of the supported standing wave modes, given by $\lambda_m = \frac{2Ln_c}{m}$, where n_c is the refractive index of the cavity material and m is the mode number. The diagram shows the three lowest-order resonant modes as an example. Inside the cavity, a gain medium is embedded to facilitate light-matter interactions, generating excitons. The thickness of this gain medium may either span the entire cavity or only a portion of it. In cases where it does not fully occupy the cavity, the remaining space is filled with buffer layers to complete the structure.

With this structure in mind, there are three key factors to consider for device fabrication: (1) microcavity design, (2) the mirrors, which determine the reflectance, and the quality factor, which is closely related to the reflectance and optical losses, and (3) gain media. In the following sections, each of these elements will be reviewed in detail.

2.5 Planar Microcavity Design

A planar microcavity typically consists of two mirrors positioned on either side of a central cavity layer, forming a structure that supports the confinement of photons through the formation of standing optical waves. The design of such a microcavity is governed by several key physical parameters that collectively determine its resonant characteristics and field confinement capabilities. One of the most critical parameters is the **cavity length**, which is generally chosen to be an integer multiple of half the effective wavelength, $\lambda/(2n)$, where λ is the free-space wavelength and n is the refrac-

tive index of the cavity medium. This condition ensures constructive interference and supports standing wave resonance at the target optical frequency.

The reflectivity (R) of the cavity mirrors plays a pivotal role in defining the **Q-factor** and photon lifetime, with high-reflectivity dielectric or metallic mirrors commonly used to achieve efficient photon confinement. The selection of materials for both the mirrors and the cavity layer significantly influences the refractive index contrast and the associated optical losses, as discussed in the preceding section. These material properties are critical in minimizing absorption and scattering losses, thereby enhancing overall cavity performance.

Precise control over the thickness of the spacer layers is essential to maintain the desired optical path length and to satisfy phase-matching conditions necessary for resonance. Furthermore, the choice of substrate material affects mechanical robustness, thermal conductivity, and optical compatibility with the active and passive layers of the microcavity. Taken together, these structural and material considerations are fundamental to realizing high finesse, strong mode confinement, and efficient light-matter interaction within planar microcavities.

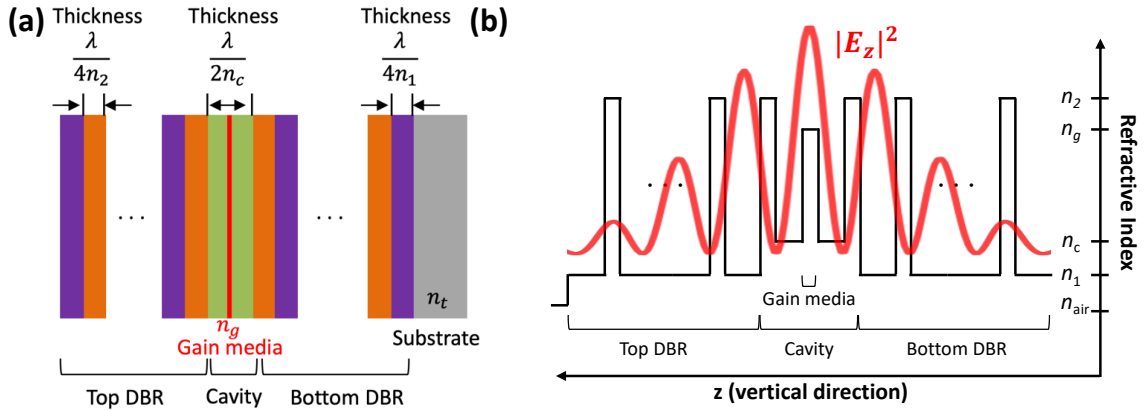


Figure 2.8: (a) Schematic of a planar microcavity consisting of a substrate, bottom **DBR**, cavity layer, and top **DBR**, where λ is the target wavelength, and n_1 , n_2 , n_c , and n_g are the refractive indices of each layer ($n_1 < n_2$). (b) Refractive index profile of the **DBR** and the spatial distribution of the electromagnetic wave intensity.

The design of the mirror for (6,5) **SWCNT** begins with the selection of suitable materials, as previously discussed, based on their reflectance properties and spectral coverage. In the case of metallic mirrors, fabrication is relatively straightforward since

they typically consist of a single metal layer. For instance, a 50 nm thick metal film can achieve reflectance values of up to approximately 99.5% at a wavelength of 1010 nm. However, to attain even higher reflectance and broader spectral control, dielectric mirrors are preferred, which necessitate the use of DBR structures.

A DBR consists of alternating layers of materials with high and low refractive indices. Each layer is typically designed with an optical thickness of $\lambda/4n$, where λ is the target wavelength and n is the refractive index of the material. This configuration satisfies the quarter-wave condition for constructive interference in reflection and destructive interference in transmission, thereby enhancing reflectivity at the design wavelength.

In a planar microcavity, the DBR structure is employed on both the top and bottom sides of a central cavity layer (Fig. 2.8(a)). The cavity layer functions as a defect state, allowing for resonant confinement of photons at the target wavelength. To support the fundamental resonant mode, the cavity thickness is typically set to $\lambda/2n_c$, where n_c is the refractive index of the cavity material (Fig. 2.8(b)). This configuration maximizes the electric field intensity at the center of the cavity due to the formation of a standing wave (Fig. 2.8(b)).

Higher-order resonant modes are also possible when the cavity thickness is increased to integer multiples of the half-wavelength optical path length, i.e., $m\lambda/2n_c$ with m is integer. Although these modes share the same resonant wavelength, the electric field intensity distribution differs, with higher-order modes generally exhibiting reduced field confinement at the center. Thus, by varying the cavity thickness, it is possible to control the electric field profile while maintaining the same resonant wavelength.

2.6 Mirrors

The mirrors enclosing the optical cavity must possess high reflectance to minimize photon losses, thereby enhancing the Q-factor of the system. This high reflectivity is intrinsically linked to the photonic stopband, the spectral range over which the mirror effectively reflects light, which is critical for ensuring sufficient photon lifetime within the cavity.

Two primary categories of mirror materials are employed in optical cavities: metallic and dielectric mirrors. Metallic mirrors typically consist of thin films of noble or reflective metals such as Au, Ag) or Al, which provide inherent reflectivity in the range

of 90–98%, depending on the metal type and film thickness. However, due to intrinsic absorption losses in metals, metallic mirrors often result in lower **Q-factor** cavities. Nevertheless, they offer broadband reflectivity across the **ultraviolet (UV)** to **infrared (IR)** spectrum and allow for relatively simple fabrication, making them suitable for broadband or tunable cavities [107].

In contrast, dielectric mirrors, most notably realized as **DBR**, consist of alternating layers of high- and low-refractive index materials. While a single dielectric layer provides minimal reflectivity, a properly designed multilayer **DBR** can achieve reflectivities exceeding 99.9% through optimization of the refractive indices and the number of layer pairs, as estimated by the following formula:

$$R_{\max}^{2N} = \left(\frac{1 - \frac{n_c}{n_t} \left(\frac{n_1}{n_2} \right)^{2N}}{1 + \frac{n_c}{n_t} \left(\frac{n_1}{n_2} \right)^{2N}} \right)^2, \quad (n_1 < n_2) \quad (2.10)$$

Here, N is the number of layer pairs, n_1 and n_2 are the refractive indices of the low- and high-index layers respectively, n_c is the refractive index of the cavity, and n_t is the refractive index of the substrate [37, 143].

These mirrors offer extremely low optical losses and excellent thermal stability, making them ideal for high-**Q-factor** applications. However, **DBR** are inherently narrow-band, with the spectral bandwidth of the stopband estimated by:

$$\Delta\lambda \approx \frac{\lambda_{\text{mid}}}{\pi} \arcsin \left(\frac{n_2 - n_1}{n_2 + n_1} \right), \quad (2.11)$$

where λ_{mid} is the center wavelength of the stopband. Additionally, their fabrication requires precise thickness control and deposition of multiple layers, increasing complexity. Despite these challenges, **DBR** are widely used in narrow-linewidth lasers and optical filters due to their superior performance in defined wavelength ranges.

The comparisons of metal and dielectric mirrors are summarized in Table 6.3.

With the mirror reflectivities, we can estimate the cavity's **Q-factor**, a dimensionless parameter that quantifies how effectively a resonator stores energy, or how sharp and narrow its resonance is. From its definition:

$$Q = 2\pi \times \frac{\text{Energy stored}}{\text{Energy lost per cycle}} = \frac{\omega_0}{\Delta\omega} = \frac{\lambda_0}{\Delta\lambda_c}, \quad (2.12)$$

Table 2.4: Mirror comparison: metal mirrors vs dielectric mirrors

	Metal	Dielectric
Structure	Thin film	Multiple alternating layers stack (DBR)
Material	Al, Au, Ag	high and low refractive indices (e.g., SiO ₂ and TiO ₂)
Reflectivity	~90-98 %	≥99.9 %
Bandwidth	Broadband (UV-IR)	Narrowband (Stopband)
Losses	High (due to the metal absorption)	Very low
Cavity Q-factor	Low	High
Fabrication Complexity	Simple	Complex
Usage	Broadband or tunable cavities, plasmonic systems	Narrow-linewidth lasers, fibers

where ω_0 is the resonance angular frequency, $\Delta\omega$ is the angular linewidth, λ_0 is the resonance wavelength, and $\Delta\lambda_c$ is the spectral linewidth.

The Q-factor can also be estimated based on the mirror reflectivities as:

$$Q \simeq \frac{\pi(R_1 R_2)^{1/4}}{1 - (R_1 R_2)^{1/2}}, \quad (2.13)$$

where R_1 and R_2 are the reflectivities of the top and bottom mirrors, respectively. Therefore, high-reflectivity mirrors are crucial for achieving high-Q-factor cavities.

However, geometric factors, especially surface roughness, also strongly influence the quality factor. Increased roughness leads to greater scattering loss, which lowers the Q-factor. For instance, it has been reported that a surface roughness of 10 nm can degrade the quality factor by up to 30% [172].

2.7 Gain Media

There are five candidates for the semiconductor gain media: inorganic materials, organic materials, transition metal dichalcogenide (TMDC)s, perovskite materials, CNTs.

The gain medium is a central component in lasers and optical amplifiers, responsible for amplifying light through the process of stimulated emission. In conventional photon lasers, the gain medium provides optical gain and enables population inversion, a critical condition for lasing. In contrast, polariton lasers do not require optical gain or population inversion. Instead, the gain medium in these systems serves to generate excitons, which are essential for enabling strong light–matter interactions and the formation of polaritons.

There are several types of gain media, including solid-state (e.g., Nd:YAG), gas-based (e.g., He-Ne), semiconductor, and liquid dye media. Among these, our focus is on semiconductor-based gain media, which will be discussed in detail in the following sections.

Typical semiconductor gain media include inorganic group III-V compounds, such as GaAs and InP, which are commonly implemented in two-dimensional (2D) or three-dimensional (3D) structures within optoelectronic devices. Due to their relatively low exciton binding energies, typically in the range of 4 to 26 meV, these materials often require cryogenic temperatures to prevent thermal dissociation in the exciton-polariton experiments [202, 140]. However, certain wide-bandgap semiconductors, such as GaN (a group III–V compound) and ZnO (a group II–VI compound), have demonstrated potential for room-temperature operation due to their high exciton binding energies [162, 149]. These materials also cover a wide range of emission wavelengths, from the UV to the NIR, ranging from approximately 360 nm to 2500 nm, depending on the specific composition. For example, GaAs emits near 870 nm. The exciton Bohr radii in these materials range from 1 to 15 nm, with GaAs having a typical value of 11.6 nm [69, 75]. The corresponding Mott density, which represents the exciton dissociation threshold, varies depending on dimensionality: approximately 10^{16} to 10^{20} cm⁻³ in 3D systems and about 10^{11} cm⁻² in 2D GaAs structures [209]. As one of the most well-studied semiconductor materials, GaAs benefits from mature fabrication technologies, allowing high-quality microcavities and excellent operational stability. Nevertheless, the relatively low exciton binding energy has motivated the search for alternative materials.

Organic semiconductors, typically composed of conjugated polymers or small molecules, are widely recognized as quasi-1D gain media due to their strong anisotropic electronic confinement and excitonic characteristics. These materials exhibit high exciton binding energies in the range of 200–1000 meV, enabling stable exciton formation even at room temperature [70, 113]. Their photoluminescence covers a broad spectral range from the UV to the visible (Vis) region, typically between 350 and 800 nm, depending on their molecular composition. The exciton Bohr radius in organic semiconductors is typically

between 2 and 5 nm, corresponding to a Mott density on the order of 10^{16} cm^{-2} . These materials are solution-processable, making them compatible with low-cost, large-area fabrication methods such as spin coating and inkjet printing, as well as integration with flexible and stretchable substrates [66]. Despite these advantages, several limitations persist. Organic semiconductors generally exhibit low charge carrier mobilities (typically $< 10^{-3} \text{ cm}^2/\text{Vs}$) [210], limiting their performance in electrically pumped devices. Additionally, their oscillator strengths are lower compared to inorganic semiconductors, reducing the efficiency of light-matter coupling. They are also prone to photobleaching and environmental degradation when exposed to oxygen, moisture, or prolonged illumination, posing a significant challenge for long-term device stability.

2D materials, particularly TMDCs such as MoS_2 , WS_2 , and WSe_2 , have emerged as promising candidates for next-generation optoelectronic devices due to their strong excitonic effects and tunable bandgaps. These materials exhibit high exciton binding energies, typically in the range of 200–900 meV, which enable the observation of stable excitons even at room temperature [35, 86, 237, 219]. Their photoluminescence spans the Vis to NIR spectral range (approximately 600–1100 nm), depending on the specific composition and thickness. TMDC monolayers possess small exciton Bohr radii ($\sim 1 \text{ nm}$ or less) and correspondingly high Mott densities, on the order of 10^{12} – 10^{14} cm^{-2} [219]. These properties facilitate strong light–matter interactions and make TMDCs suitable for applications in nanolasers, light-emitting diodes, and polariton condensates. However, despite their attractive optical characteristics, the practical deployment of TMDCs faces challenges related to large-area synthesis, layer uniformity, and integration with existing photonic and electronic platforms.

Perovskites, an emerging class of semiconductor materials, have garnered significant attention for their tunable optoelectronic properties and facile solution-processable fabrication. These materials can be synthesized in both 2D and 3D crystal structures. They exhibit moderate to high exciton binding energies, typically ranging from 30 to 540 meV, enabling excitonic effects even at or near room temperature [152, 238]. The photoluminescence of perovskites spans a broad spectral region from the UV to the NIR, approximately 380–950 nm, depending on the halide composition and dimensionality [65, 34]. The exciton Bohr radius is generally in the range of 1–3 nm in 2D structures and 2–10 nm in 3D counterparts [180, 238]. Correspondingly, their Mott densities are estimated to be around 10^{13} cm^{-2} for 2D structures and 10^{18} cm^{-3} for 3D structures [163, 238]. These properties make perovskites attractive for applications in light-emitting diodes, lasers, and photodetectors. Nevertheless, perovskite materials face significant challenges in long-term stability, particularly under exposure to humidity, oxygen, and light. Furthermore, many of the high-performing perovskites

incorporate lead (Pb), raising environmental and toxicity concerns [134]. Continued research is aimed at improving their environmental robustness and developing lead-free alternatives without compromising optoelectronic performance.

CNTs, particularly SWCNT, have been extensively investigated as quasi-1D materials for optoelectronic applications. Due to their 1D electronic structure, SWCNTs exhibit pronounced excitonic effects with high exciton binding energies in the range of 300–500 meV [195, 142, 15]. Their photoluminescence spans the NIR region, typically from 900 to 2100 nm, depending on their chirality and diameter [20, 106]. The exciton Bohr radius in SWCNTs is estimated to be around 0.5–2 nm, leading to high Mott densities on the order of 10^{13} – 10^{14} cm⁻² [91, 8, 190]. The strong confinement and reduced dielectric screening in SWCNTs result in highly localized excitons and enhanced light–matter interactions. Moreover, their direct bandgap and unique electronic structure allow for bandgap tunability through chirality selection or strain engineering, without the need to alter chemical composition. These features make SWCNTs compelling candidates for use as laser gain media, a topic that will be discussed in detail later in this work.

Table 2.5: Comparison of gain media

	Inorganic	Organic (Polymer)	TMDC	Perovskite	SWCNT
Dimension	2D/3D	1D	2D	2D/3D	1D
Binding Energy	4-26 meV	200-1000 meV	200-900 meV	30-540 meV	300-500 meV
Emission Range	360-2500 nm UV-Vis-NIR (GaAs 870 nm)	350-800 nm UV-Vis	600-1100 nm Vis-NIR	380-950 nm UV-Vis-NIR	900-2100 nm NIR
Exciton Bohr Radius	1-15 nm	2-5 nm	~1 nm	1-3 nm (2D) 2-10 nm (3D)	0.5-2 nm
Mott Density	$\sim 10^{16}$ - 10^{20} cm ⁻³ (2D GaAs $\sim 10^{11}$ cm ⁻²)	$\sim 10^{16}$ cm ⁻²	$\sim 10^{12}$ - 10^{14} cm ⁻²	$\sim 10^{14}$ cm ⁻² (2D) $\sim 10^{18}$ cm ⁻³ (3D)	$\sim 10^{13}$ - 10^{14} cm ⁻²
Remark	Cryogenic Fab. difficulty	Localization Bleaching issue	Low throughput Size limit	Material stability	Tunable wavelength Localized excitons

Based on the comprehensive review of resonator architectures, the FP cavity has been selected as the platform for optical device development aimed at demonstrating a new type of laser. In particular, SWCNTs have been chosen as the gain medium due to their exceptional potential for NIR semiconductor laser applications. Unlike traditional

semiconductor materials, SWCNTs offer broadband and tunable emission across the NIR region, which remains a challenge for many conventional semiconductors.

A significant advantage of SWCNTs lies in their material adaptability. Once a reliable fabrication and processing recipe is established, the emission wavelength can be tuned without modifying the overall fabrication methodology, simply by selecting SWCNTs with the desired chirality. This stands in contrast to conventional semiconductors, where material, specific processes are typically required for different wavelength ranges.

Given these strengths, SWCNTs represent a promising path forward in the pursuit of compact, tunable NIR lasers. The following sections will provide a detailed review of the optical and electronic properties of SWCNTs, followed by experimental implementation within the FP cavity design.

Chapter 3

Single-Walled Carbon Nanotubes As a Gain Medium

The discovery of CNT in soot by S. Iijima in 1991 [100] sparked a new era in nanotechnology. Since then, CNT have attracted considerable interest and have been extensively investigated owing to their exceptional multifunctional properties. As illustrated in Fig. 3.1, CNTs demonstrate outstanding electrical, chemical, biological, mechanical, optical, and thermal characteristics. These unique attributes position CNTs as a versatile material platform with significant potential across a broad spectrum of technological domains, including nanoelectronics, materials science, energy storage, and biomedical applications [99].

The electronic properties of CNT are determined by their chirality and diameter, allowing them to behave as either metals or semiconductors. *Electrically*, CNTs can behave either as metals or semiconductors, depending on their chirality and diameter. They support remarkably high current densities on the order of $\sim 4 \times 10^9$ A/cm², which exceeds that of conventional Cu conductors by more than three orders of magnitude [92]. In addition, their carrier mobility surpasses that of crystalline silicon by a factor of over 56, making them highly attractive for high-performance nanoelectronic devices [55]. *Chemically*, CNTs offer a high surface area that can be tailored through covalent or non-covalent functionalization, enhancing their reactivity, dispersibility, and compatibility with a variety of matrices [12]. *Biologically*, they are considered non-toxic and biocompatible under appropriate conditions, which supports their use in drug delivery, biosensing, and other biomedical applications [189]. *Mechanically*, CNTs demonstrate extraordinary tensile strength, reaching up to 25 GPa, which is approximately ten times higher than that of structural steel [198]. Their Young's mod-

ulus approaches 1.2 TPa, approximately 12,000 times greater than that of elastomeric materials such as rubber [67], highlighting their utility in advanced composites and structural reinforcements. **Optically**, semiconducting CNTs exhibit direct bandgaps that are highly tunable as a function of their chirality and diameter, allowing emission and absorption in the NIR region between 900 and 1800 nm. This feature is particularly relevant for optoelectronic applications including photodetectors, bio-imaging, and light-emitting devices. **Thermally**, CNTs possess exceptional heat transport capabilities, with thermal conductivities reaching up to ~ 6000 W/mK, approximately 16 times greater than that of copper [181]. They also exhibit excellent thermal stability, maintaining structural integrity up to 2800 °C in vacuum and up to 750 °C in ambient air [204], making them suitable for use in extreme environments.

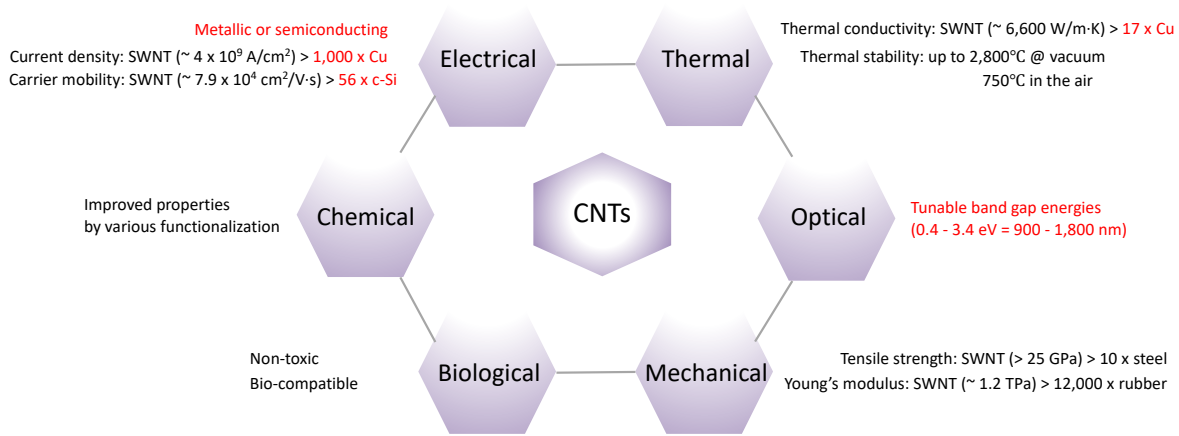


Figure 3.1: Carbon nanotubes (CNTs) are recognized as highly multifunctional materials due to their exceptional electrical [92, 55], chemical [12], biological [189], mechanical [198, 67], optical, and thermal [181, 204] properties.

Among the diverse and remarkable properties of CNT, their optical characteristics are of particular interest in this study owing to their promising potential in quantum nanophotonic devices, particularly light-emitting systems. In order to contextualize their optical behavior, we first present a concise overview of the fundamental material structure and intrinsic electronic properties of CNT.

3.1 Physical Structure of Carbon Nanotubes

Carbon, one of the most versatile elements in the periodic table, belongs to group four in the periodic table and has an atomic number of six. Carbon has two electrons in the 1s core level and four valence electrons distributed in the 2s and 2p orbitals, as illustrated in Fig. 3.2(a). The valence electrons in the 2s and 2p orbitals are primarily responsible for chemical bonding and hybridization, as shown in Fig. 3.2(b). This electronic configuration allows carbon to undergo sp , sp^2 , and sp^3 hybridizations, which in turn enable the formation of a diverse range of molecular and crystal structures (Fig. 3.2(c)). With four valence electrons, carbon gives rise to numerous allotropes across all dimensions, including fullerenes (0D), CNTs (1D), graphene (2D), amorphous carbon (3D), graphite (3D), and diamond (3D). Among these, CNTs have emerged as one of the most promising nanostructures because they exhibit exceptional electrical, mechanical, and optical properties, positioning them at the forefront of both fundamental research and advanced technological applications. Although prior research and publications on CNTs existed, widespread scientific interest was catalyzed by Sumio Iijima's 1991 report on MWCNTs synthesized via arc-discharge methods [100], and was further intensified by the subsequent discovery of SWCNTs in 1993 [101]. CNTs are hollow, cylindrical nanostructures composed of carbon atoms arranged in a hexagonal lattice, effectively resembling seamless, rolled-up graphene sheets.

CNT are members of the sp^2 -hybridized carbon material family, sharing fundamental structural and electronic features with graphene and graphite. In this hexagonal framework, each carbon atom forms three strong covalent σ -bonds with neighboring atoms, resulting in a planar honeycomb lattice. The remaining unhybridized p_z orbital in Fig. 3.2(c) on each carbon atom overlaps with those of adjacent atoms to form a delocalized π -electron system, which facilitates exceptional electrical conductivity, chemical stability, and mechanical stiffness. The distinctive topology of CNT, formed by seamlessly rolling a 2D graphene sheet into a high-aspect-ratio quasi-1D cylindrical nanostructure, introduces pronounced quantum confinement and curvature, induced π - σ hybridization effects. These structural deformations break the symmetry of the graphene band structure, giving rise to unique electronic behaviors, including metallic or semiconducting characteristics depending on chirality, which are not present in their planar graphene counterparts [182, 51].

A CNT can be conceptualized as a rolled-up sheet of graphene, where the direction and angle of rolling determine its structural type and properties. This process is mathematically described using two vectors: the chiral vector ($\vec{C}_h$) and the translation vector ($\vec{T}$),

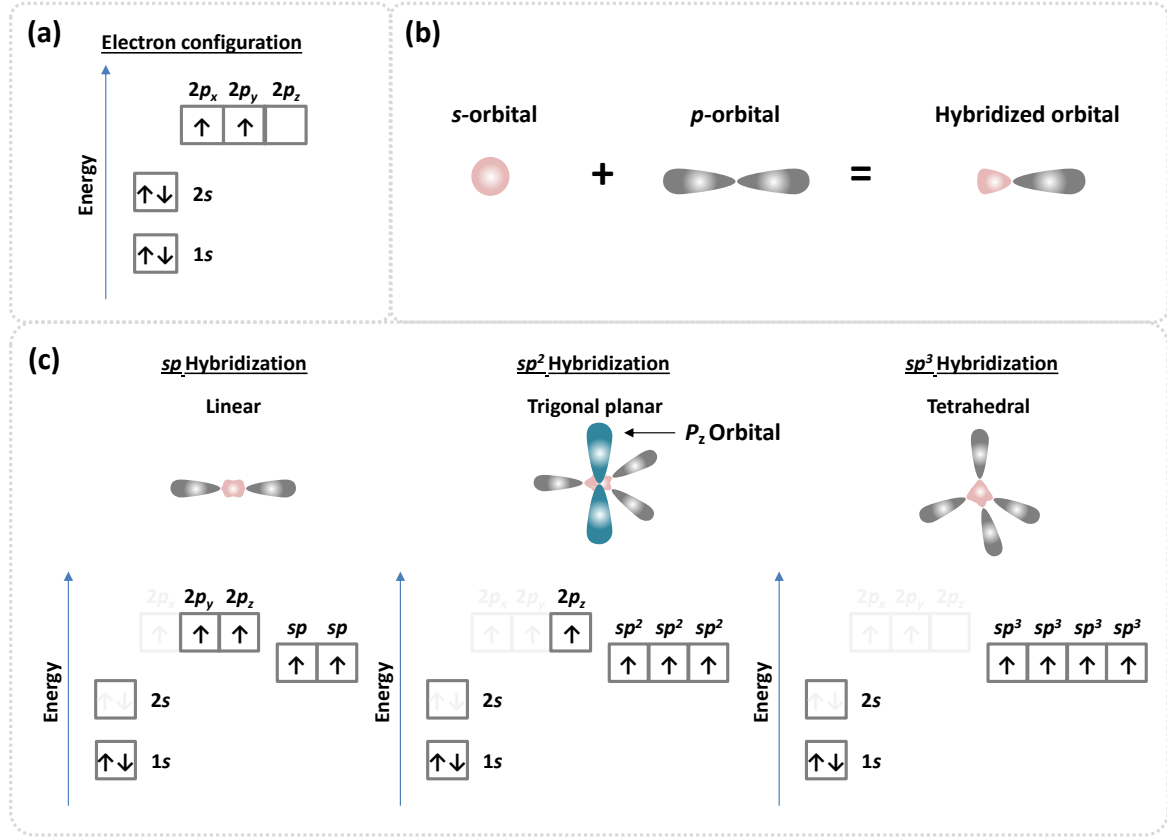


Figure 3.2: Carbon electron configurations and hybridization: (a) Ground-state configuration; (b) Formation of hybrid orbitals from s and p orbitals; (c) Electron configurations for sp , sp^2 , and sp^3 hybridizations, with arrows indicating spin and orbital shape revised from [228].

$$\begin{aligned}\vec{C}_h &= n\vec{a}_1 + m\vec{a}_2, \\ \vec{T} &= t_1\vec{a}_1 + t_2\vec{a}_2,\end{aligned}\tag{3.1}$$

where $\vec{a}_1$ and $\vec{a}_2$ are the primitive lattice vectors of graphene, and (n, m) are integers that define the chirality of the nanotube. The coefficients t_1 and t_2 are given by:

$$t_1 = \frac{2m + n}{d_R}, \quad t_2 = -\frac{2n + m}{d_R},\tag{3.2}$$

where d_R is defined as the greatest common divisor (gcd) of the two integers $2n + m$ and $2m + n$, i.e.,

$$d_R = \gcd(2n + m, 2m + n). \quad (3.3)$$

The value of d_R is related to the difference $(n - m)$ as follows:

- If $(n - m)$ is a multiple of 3, then $d_R = \gcd(n, m)$;
- Otherwise, $d_R = 3 \times \gcd(n, m)$.

The chiral vector $\vec{C}_h$ defines the circumference of the nanotube. The translation vector $\vec{T}$, determined by integers t_1 and t_2 , governs the periodicity along the nanotube's axis, ensuring that the graphene sheet repeats periodically along the length of the tube in Fig 3.4(a). Together, these vectors define the geometric structure and influence the electronic properties of the nanotube, including its diameter, chirality, and electronic band structure [182].

CNTs are broadly categorized into two principal structural forms: SWCNT and MWCNT, as illustrated in Fig. 3.4(b). A SWCNT consists of a single graphene sheet rolled seamlessly into a hollow cylindrical structure, typically exhibiting diameters in the range of 0.4 to 2 nm [101, 51]. The electronic properties of SWCNT are fundamentally determined by their chirality, which is characterized by a pair of integers (n, m) known as chiral indices. These indices not only define the wrapping vector of the graphene sheet but also dictate the nanotube's diameter and their correspond angle defined in Fig. 3.3, given by the expression

$$d = \frac{a}{\pi} \sqrt{n^2 + nm + m^2} \quad (3.4)$$

$$\cos \theta = \frac{\vec{C}_h \cdot \vec{a}_1}{|\vec{C}_h| |\vec{a}_1|} = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}. \quad (3.5)$$

where $a = 0.246 \text{ nm}$ is the lattice constant of graphene.

The chirality (n, m) directly determines the electronic nature of the nanotube: if $n - m = 3k$ (where k is an integer), the SWCNT is metallic (red dots in Fig. 3.3); otherwise, it is semiconducting (blue dots in Fig. 3.3) with a finite bandgap [182]. This

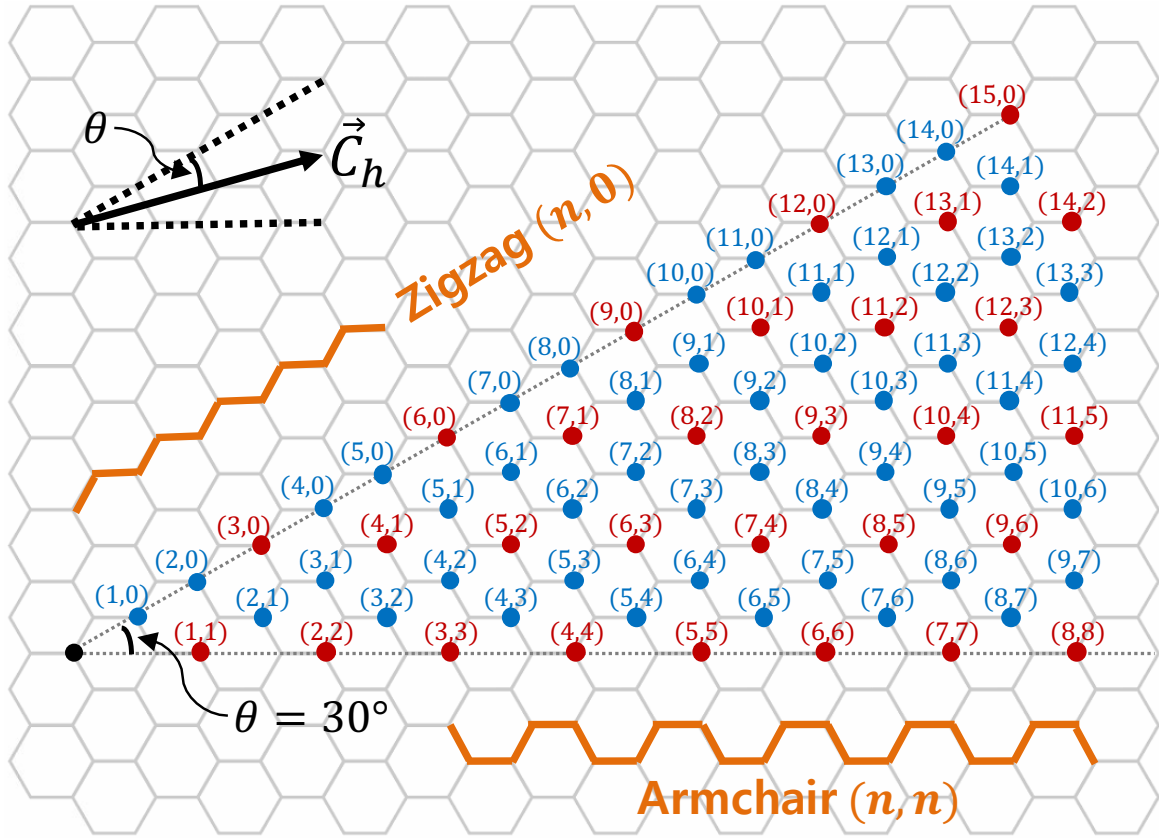


Figure 3.3: Series of chiral vectors represented on a hexagonal lattice, illustrating the (n, m) indexing scheme used to define the structure and chirality of SWCNTs adapted from [228].

structure-dependent electronic behavior makes SWCNTs highly tunable and useful for a variety of nanoelectronic and optoelectronic applications. Chirality further classifies SWCNT into three structural types: *armchair* ($n = m$), which are always metallic and exhibit high symmetry and zero bandgap; *zigzag* ($m = 0$), which may be metallic or semiconducting depending on the value of n ; and *chiral* ($n \neq m \neq 0$), which generally exhibit semiconducting behavior and possess helical symmetry [182]. The ability to tailor the bandgap through chirality and diameter makes semiconducting SWCNT highly attractive for applications in nanoscale electronics and optoelectronics, including field-effect transistors, photodetectors, and light-emitting devices [200, 59].

In contrast, MWCNT are composed of multiple concentric SWCNTs, with an inter-

layer spacing of approximately 0.34 nm, which is comparable to the spacing between adjacent graphene layers in bulk graphite [100, 90]. Due to the presence of multiple walls, MWCNTs exhibit enhanced mechanical robustness and higher thermal conductivity compared to their single-walled counterparts [203]. Although interlayer coupling and charge screening in MWCNTs can complicate their electronic characterization, advances in synthesis and separation techniques now allow for selective isolation of semiconducting–semiconducting configurations. In such structures, excitonic recombination predominantly occurs in the outermost or larger-diameter walls, where optical transitions are more accessible and less perturbed by interlayer interactions [39, 206, 231]. Despite this limitation, MWCNTs remain valuable in applications requiring high strength, durability, and thermal management, such as composite materials, interconnects, and thermal interface layers.

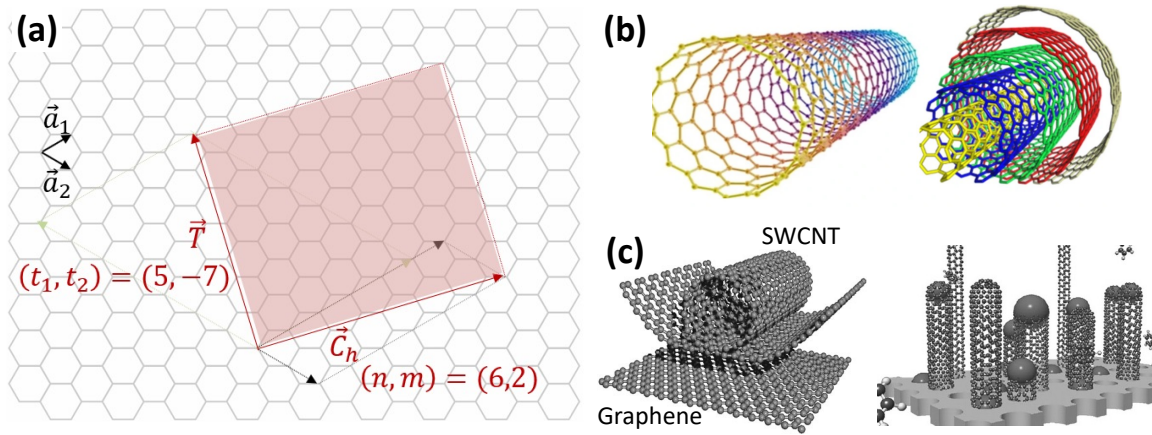


Figure 3.4: (a) An example of a single-walled carbon nanotube (SWCNT) with (6,2) chirality unfolded onto a 2D hexagonal graphene sheet, showing the chiral vector $\vec{C}_h$ and translation vector $\vec{T}$ revised from [228]. (b) Schematic illustration of a SWCNT (left) and a multi-walled carbon nanotube (MWCNT) (right) adapted from [50]. (c) Conceptual diagram showing the formation of a SWCNT from a graphene sheet (left) and a practical example of SWCNT growth using a catalyst (right) reprinted from [3].

Although theoretical models often depict CNT formation as the seamless rolling of a graphene sheet into a cylindrical geometry, as illustrated in Fig. 3.4(c, left), this idealized representation does not fully capture the complexities of practical synthesis. In reality, CNTs are predominantly fabricated via CVD, wherein transition metal nanoparticles (e.g., Fe, Ni, Co) serve as nucleation sites that guide the directional growth of nan-

otubes under precisely controlled thermal and chemical environments, as shown in Fig. 3.4(c, right) [44]. This bottom-up approach enables scalable and selective production of both SWCNTs and MWCNTs with tunable diameters, chiralities, and lengths. The structural and electronic properties of the resulting nanotubes are highly sensitive to synthesis conditions, including catalyst composition, growth temperature, carbon feed-stock, and substrate properties [230, 226, 144]. Accordingly, fine control over these parameters is essential for tailoring CNT functionalities in device applications.

3.2 Electronic Structures of Single-Walled Carbon Nanotubes

SWCNTs exhibit exceptional optical and electronic properties arising from their quasi-1D geometry and quantum confinement effects. In contrast to bulk materials, which feature continuous energy bands, SWCNTs display singular DOS due to quantization along the circumferential direction. This results in pronounced van Hove singularities in the electronic DOS, which give rise to sharp optical transitions observable in absorption and photoluminescence spectra. The energies and intensities of these transitions are strongly dependent on the nanotube's chirality (n, m) and diameter, making optical spectroscopy an essential tool for SWCNT characterization [20, 52].

As previously discussed, the electronic nature of a SWCNT, metallic or semiconducting, is determined by its chiral indices (n, m) . The electronic structure and DOS can be analytically estimated using a zone-folding approach based on the graphene band structure, calculated through a nearest-neighbor tight-binding approximation from the secular equation with a wavefunction Ψ with Bloch's theorem.

Secular Equation

In a crystal, due to its translational symmetry, a wavefunction Ψ must satisfy Bloch's theorem along any lattice vector $\vec{a}_j$:

$$T_{\vec{a}}\Psi = e^{i\vec{k}\cdot\vec{a}_j}\Psi, \quad (3.6)$$

where $T_{\vec{a}}$ is the translation operator, $\vec{k}$ is the wavevector, and $\vec{a}_j$ are the lattice vectors ($j = 1, 2, 3$). A Bloch function $\Phi_j(\vec{k}, \vec{r})$ is defined as

$$\Phi_j(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \varphi_j(\vec{r} - \vec{R}), \quad (j = 1, \dots, n) \quad (3.7)$$

where φ_j is the atomic orbital, $\vec{R}$ labels atomic positions, N is the number of unit cells, and n is the number of orbitals per unit cell. This Bloch function satisfies the translational symmetry:

$$\Phi_j(\vec{k}, \vec{r} + \vec{a}) = e^{i\vec{k} \cdot \vec{a}} \Phi_j(\vec{k}, \vec{r}). \quad (3.8)$$

The eigenfunction $\Psi_j(\vec{k}, \vec{r})$ is a linear combination of Bloch functions:

$$\Psi_j(\vec{k}, \vec{r}) = \sum_{j'=1}^n C_{jj'}(\vec{k}) \Phi_{j'}(\vec{k}, \vec{r}), \quad (3.9)$$

where $C_{jj'}(\vec{k})$ are coefficients to be determined. The energy eigenvalue is given by

$$E_j(\vec{k}) = \frac{\langle \Psi_j | \mathcal{H} | \Psi_j \rangle}{\langle \Psi_j | \Psi_j \rangle}. \quad (3.10)$$

Substituting Eq. 3.9 into Eq. 3.10 yields:

$$E_i(\vec{k}) = \frac{\sum_{jj'} C_{ij}^* C_{ij'} \langle \Phi_j | \mathcal{H} | \Phi_{j'} \rangle}{\sum_{jj'} C_{ij}^* C_{ij'} \langle \Phi_j | \Phi_{j'} \rangle} = \frac{\sum_{jj'} C_{ij}^* C_{ij'} \mathcal{H}_{jj'}(\vec{k})}{\sum_{jj'} C_{ij}^* C_{ij'} \mathcal{S}_{jj'}(\vec{k})}, \quad (3.11)$$

where $\mathcal{H}_{jj'} = \langle \Phi_j | \mathcal{H} | \Phi_{j'} \rangle$ is the Hamiltonian matrix and $\mathcal{S}_{jj'} = \langle \Phi_j | \Phi_{j'} \rangle$ is the overlap matrix.

Minimizing $E_i(\vec{k})$ with respect to C_{ij}^* leads to

$$\sum_{j'=1}^n \mathcal{H}_{jj'}(\vec{k}) C_{ij'} = E_i(\vec{k}) \sum_{j'=1}^n \mathcal{S}_{jj'}(\vec{k}) C_{ij'}. \quad (3.12)$$

This yields the generalized eigenvalue problem:

$$\mathcal{H}\mathbf{C}_i = E_i(\vec{k})\mathcal{S}\mathbf{C}_i, \quad (3.13)$$

where $\mathbf{C}_i$ is the column vector of coefficients. To find nontrivial solutions, the determinant must vanish:

$$\det[\mathcal{H} - E_i(\vec{k})\mathcal{S}] = 0. \quad (3.14)$$

This is the secular equation, determining the allowed energy bands $E_i(\vec{k})$ in the crystal.

Hamiltonian

According to the secular equation method, 2×2 matrices for both the transfer integral matrix $\mathcal{H}$ and the overlap integral matrix $\mathcal{S}$ are constructed to determine the energy bands. In graphene, the unit cell, shown as a red-grayed diamond in Fig. 3.5, consists of two carbon atoms labeled A and B, forming the basis of a two-band model.

The Hamiltonian matrix $\mathcal{H}_{ij}$ includes:

- Diagonal terms $\mathcal{H}_{AA}, \mathcal{H}_{BB}$ — interaction between same sublattice atoms
- Off-diagonal terms $\mathcal{H}_{AB}, \mathcal{H}_{BA}$ — interaction between different sublattice atoms

$$\mathcal{H} = \begin{pmatrix} \mathcal{H}_{AA} & \mathcal{H}_{AB} \\ \mathcal{H}_{BA} & \mathcal{H}_{BB} \end{pmatrix}. \quad (3.15)$$

Diagonal Terms

The diagonal components describe interactions in Fig. 3.5(a) between an atom and its equivalents in the same sublattice. The dominant contribution comes from the on-site energy, with smaller corrections from further neighbors. Approximating using only the dominant term:

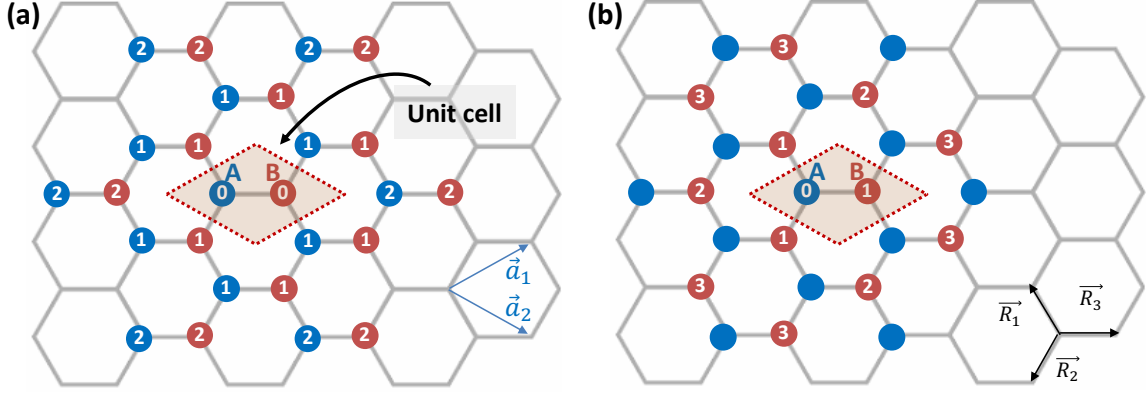


Figure 3.5: Hexagonal lattice structure of graphene in real space. (a) Nearest neighbors labeled by distance levels from carbon atoms in the unit cell, relevant for the diagonal terms of the Hamiltonian. (b) Nearest neighbors relative to an A-site atom in the unit cell, indicating interactions with B-site atoms for the off-diagonal terms in the Hamiltonian reproduced from [228].

$$\mathcal{H}_{AA}(r) = \frac{1}{N} \sum_{R, R'} e^{i\vec{k} \cdot (R - R')} \langle \varphi_A(r - R') | \mathcal{H} | \varphi_A(r - R) \rangle, \quad (3.16)$$

$$\approx \epsilon_{2p}, \quad (3.17)$$

$$= \mathcal{H}_{BB}(r) \quad (3.18)$$

Off-Diagonal Terms

These terms represent the interaction between atoms in different sublattices. Atom A interacts with three nearest-neighbor B atoms located at vectors $\vec{R}_i$ (Fig. 3.5(b)).

$$\mathcal{H}_{AB}(r) = \frac{1}{N} \sum_{i=1}^3 \sum_R e^{i\vec{k} \cdot \vec{R}_i} \langle \varphi_A(r - R) | \mathcal{H} | \varphi_B(r - R_i) \rangle, \quad (3.19)$$

$$\approx t \left(e^{i\vec{k} \cdot \vec{R}_1} + e^{i\vec{k} \cdot \vec{R}_2} + e^{i\vec{k} \cdot \vec{R}_3} \right), \quad (3.20)$$

$$= t f(k) = \mathcal{H}_{BA}^*(r) \quad (3.21)$$

with position vectors:

$$\vec{R}_1 = \left(-\frac{a}{2\sqrt{3}}, \frac{a}{2}\right), \quad \vec{R}_2 = \left(-\frac{a}{2\sqrt{3}}, -\frac{a}{2}\right), \quad \vec{R}_3 = \left(\frac{a}{\sqrt{3}}, 0\right).$$

and the phase factor becomes:

$$f(k) = e^{i\vec{k}\cdot\vec{R}_1} + e^{i\vec{k}\cdot\vec{R}_2} + e^{i\vec{k}\cdot\vec{R}_3}, \quad (3.22)$$

$$= e^{\frac{ik_x a}{\sqrt{3}}} + 2e^{-\frac{ik_x a}{2\sqrt{3}}} \cos\left(\frac{k_y a}{2}\right). \quad (3.23)$$

Hamiltonian and Overlap Matrices

Combining the results, the matrices become:

$$\mathcal{H} = \begin{pmatrix} \epsilon_{2p} & tf(k) \\ tf(k)^* & \epsilon_{2p} \end{pmatrix}, \quad \mathcal{S} = \begin{pmatrix} 1 & sf(k) \\ sf(k)^* & 1 \end{pmatrix}. \quad (3.24)$$

Energy Dispersion

Solving the secular equation $\det(\mathcal{H} - E\mathcal{S}) = 0$, we obtain:

$$E_{g2D}(\vec{k}) = \frac{\epsilon_{2p} \pm tw(\vec{k})}{1 \pm sw(\vec{k})}, \quad (3.25)$$

with:

$$w(\vec{k}) = |f(\vec{k})| = \sqrt{1 + 4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)}. \quad (3.26)$$

In the simplified case $\epsilon_{2p} = 0, s = 0$, the dispersion reduces and the energy dispersion relation for pristine [2D](#) graphene is given by:

$$E_{g2D}(k_x, k_y) = \pm t \sqrt{1 + 4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{3k_y a}{2}\right) + 4\cos^2\left(\frac{3k_y a}{2}\right)}, \quad (3.27)$$

where t is the nearest-neighbor hopping energy (typically ~ 2.7 eV, and $a = 0.249$ nm is the effective lattice constant for SWCNT, slightly larger than that of planar graphene ($a = 0.246$ nm), due to curvature-induced bond length relaxation [182].

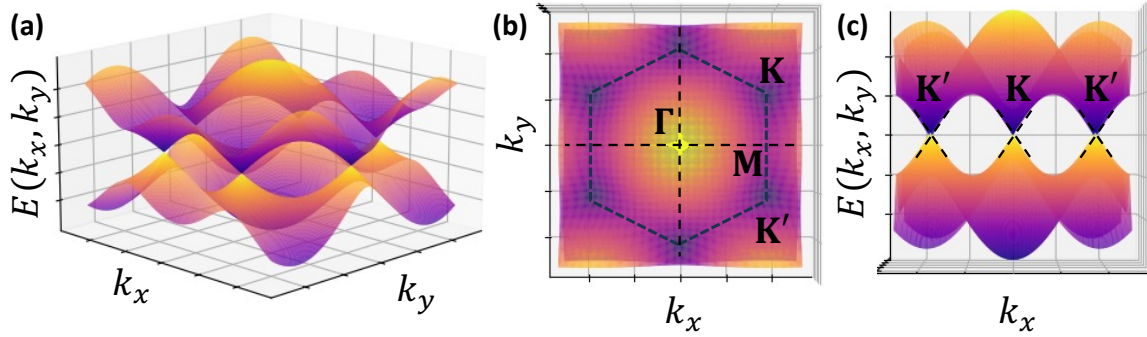


Figure 3.6: Energy dispersion of graphene with $\epsilon_{2p} = 0$, $s = 0$, and $t = 1$. The linear dispersion at the Dirac points signifies massless Dirac fermions. (a) 3D representation of the first Brillouin zone. (b) First Brillouin zone highlighting high-symmetry points: Γ , K , K' , and M . (c) Projection onto the (k_x, k_y) plane near the K and K' points.

Figure 3.6 presents the energy dispersion characteristics of graphene with Eq. 3.27 under the simplifying assumptions of $\epsilon_{2p} = 0$, $s = 0$, and $t = 1$. These parameters respectively eliminate on-site energy contributions, overlap integrals, and normalize the hopping energy, allowing a clear visualization of the intrinsic band structure of ideal graphene.

First, 3D representation of the energy bands across the first Brillouin zone is in Fig. 3.6(a). The conduction and valence bands intersect at six discrete points—three of which are inequivalent due to lattice symmetry—referred to as the **Dirac points** (labeled as K and K'). At these points, the energy varies linearly with wave vector, leading to a conical shape known as a Dirac cone. This linear dispersion signifies that the low-energy excitations in graphene behave as massless Dirac fermions, resulting in extraordinary electrical properties, such as ultrahigh mobility and zero effective mass. Figure 3.6(b) displays a top-down view of the first Brillouin zone with emphasis on high-symmetry points, including the center point Γ , the corners K and K' , and the midpoints of the edges M . These symmetry points play a central role in defining the electronic and vibrational properties of the material. Another projection of the energy dispersion onto the (k_x, k_y) plane is in Figure 3.6(c), zoomed in near the K and K' points. The conical intersection of the conduction and valence bands in this region is a key hallmark of graphene's electronic structure and is central to its designation as a zero-gap

semiconductor or semimetal.

From 2D Graphene to 1D Subbands in Single-Walled Carbon Nanotubes - Zone Folding Approach

The electronic band structure of a [SWCNT](#) can be derived from that of graphene by imposing periodic boundary conditions along the nanotube's circumferential (or chiral) direction. This quantization constraint effectively restricts the allowed electronic wavevectors to discrete values around the tube's circumference, while retaining continuous translational symmetry along its axis. This results in a set of [1D](#) subbands derived from slicing the graphene Brillouin zone along discrete lines determined by the chiral vector $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$. The energy dispersion for the [SWCNT](#) then becomes:

$$E_{\text{SWCNT}}(k) = E_{g2D} \left(k \frac{\mathbf{K}_2}{|\mathbf{K}_2|} + \mu \mathbf{K}_1 \right), \quad \left(\mu = 0, \dots, N-1; -\frac{\pi}{T} < k < \frac{\pi}{T} \right), \quad (3.28)$$

where $\mathbf{K}_1 = \frac{1}{N}(-t_2\vec{b}_1 + t_1\vec{b}_2)$ and $\mathbf{K}_2 = \frac{1}{N}(m\vec{b}_1 - n\vec{b}_2)$ are the reciprocal lattice vectors of the nanotube (with reciprocal lattice vectors $b_1 = \left(\frac{1}{\sqrt{3}}, 1\right)\frac{2\pi}{a}$ and $b_2 = \left(\frac{1}{\sqrt{3}}, -1\right)\frac{2\pi}{a}$ and length of unit vector $a = \sqrt{3}a_{\text{C-C}} = 2.49 \text{ \AA}$), μ is the quantum number arising from the periodic boundary condition imposed along the circumference (i.e., the chiral vector direction), N denotes the number of quantized subbands in this direction ($N = \frac{2(n^2+m^2+nm)}{d_R}$), and T is the length of the translation unit cell along the nanotube axis [182, 177]. This zone-folding approach, derived from the graphene band structure, successfully predicts the emergence of van Hove singularities in the [DOS](#) and provides a first approximation of the interband optical transition energies. However, this model significantly overestimates the transition energies because it is based solely on the electronic band structure of graphene and neglects excitonic interactions. In reality, strong excitonic effects in [SWCNTs](#) lead to a substantial redshift of the optical transition energies, which must be taken into account for accurate description and interpretation of experimental spectra [195].¹

¹van Hove singularities refer to divergences in the free-carrier density of states in one-dimensional systems. Excitonic resonances observed in SWCNTs occur at energies below these singularities and correspond to discrete bound states formed by electron-hole Coulomb interactions. The term “van Hove singularities” is often extended to describe these optical transitions for simplicity.

These theoretical predictions are critical for interpreting experimental spectroscopy data, including absorption, photoluminescence, and Raman scattering measurements.

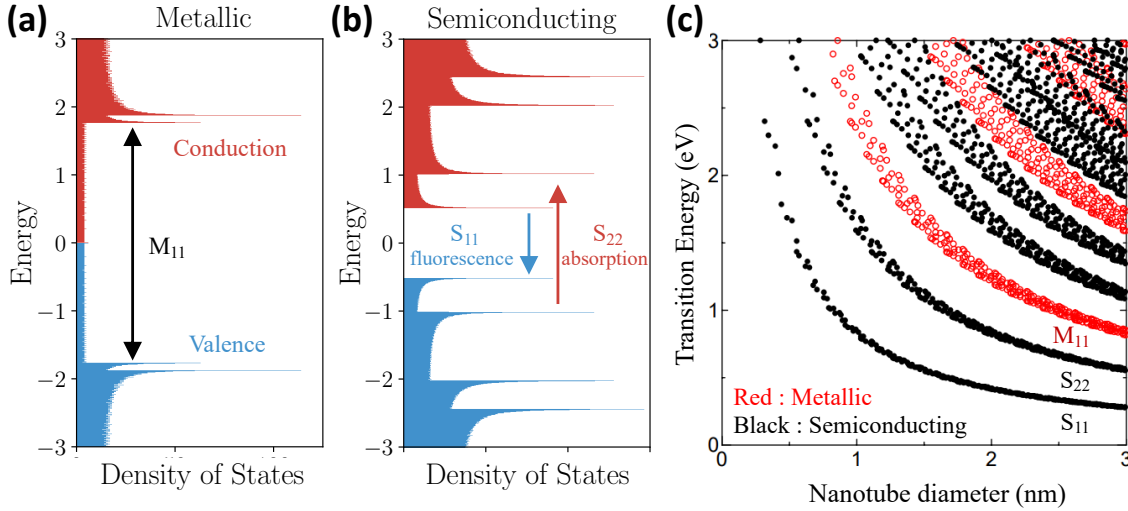


Figure 3.7: Representative DOS for (a) a metallic SWCNT and (b) a semiconducting SWCNT, highlighting the characteristic van Hove singularities for (6,5) chirality. (c) Kataura plot showing the optical transition energies (E_{ii}) of SWCNT as a function of nanotube diameter, distinguishing between metallic (M_{ii} , red) and semiconducting (S_{ii} , black) species adapted from [4].

The DOS profiles for representative metallic and semiconducting SWCNTs are shown in Fig. 3.7(a) and (b), respectively. In metallic SWCNTs, the conduction and valence bands are continuous at the Fermi level, whereas semiconducting SWCNTs exhibit a distinct bandgap separating the two. Both types display pronounced peaks in the DOS, known as van Hove singularities, which arise from the 1D nature of their electronic structure [182, 51]. The next section will explore the optical properties in relation to the underlying electronic structures of SWCNTs.

3.3 Optical Properties of Single-Walled Carbon Nanotubes

Optical transitions in SWCNTs occur between corresponding valence and conduction subbands, denoted as E_{ii} , where i is the subband index. For example, E_{11} and E_{22} represent the first and second subband transitions, respectively. These transitions are

further classified as M_{ii} for metallic nanotubes and S_{ii} for semiconducting nanotubes. Although metallic nanotubes have no band gap, M_{ii} transitions remain optically allowed due to the presence of sharp van Hove singularities near the Fermi level, which enhance optical absorption as illustrated in Fig. 3.7(c) [4]. This well-known Kataura plot maps the transition energy as a function of nanotube diameter. Each family of transitions (M_{ii} or S_{ii}) follows a distinct trend. For semiconducting SWCNTs, the bandgap (E_g) can be approximated by:

$$E_g = \frac{2\hbar v_F}{d} = \frac{4\pi\hbar v_F}{|\vec{C}_h|}, \quad (3.29)$$

where v_F is the Fermi velocity (approximately 10^6 m/s) and d is the nanotube diameter of a given SWCNT.

This plot indicates that interband transitions occur only between subbands of the same index due to optical selection rules. Each μ in Eq. 3.28 corresponds to a 1D subband obtained by slicing the 2D graphene Brillouin zone. Transitions with $\Delta\mu = 0$ are allowed under parallel polarization (light polarized along the nanotube axis), while $\Delta\mu \neq 0$ transitions are generally forbidden. Note that these selection rules arise from the symmetry of the optical transition matrix element:

$$M_{cv} \propto \langle \psi_c | \vec{E} \cdot \vec{r} | \psi_v \rangle, \quad (3.30)$$

where $\vec{E} \cdot \vec{r}$ the electric dipole operator ($\vec{E}$: electric field of the incident light, $\vec{r}$: position operator), and ψ_v , ψ_c are the valence and conduction band wavefunctions, respectively. The wavefunctions near the K-point of graphene are written as:

$$\psi_k(\vec{r}) = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ \pm \exp(i\theta_{\vec{k}}) \end{bmatrix} \exp(i\vec{k} \cdot \vec{r}) = u_{\vec{k}}(\vec{r}) \exp(i\vec{k} \cdot \vec{r}), \quad (3.31)$$

where $\theta_{\vec{k}} = \tan^{-1}(k_y/k_x)$, and $\pm$ denotes conduction and valence bands, respectively. When graphene is rolled into a SWCNT, the wavevector decomposes as:

$$\vec{k} = k_z \hat{z} + k_{\perp}^{(\mu)} \hat{\perp}, \quad (3.32)$$

where $\hat{z}$ is the nanotube axis direction (same as $\mathbf{K}_2$ direction), $\hat{\perp}$ is the circumferential direction (same as $\mathbf{K}_1$ direction), and $k_{\perp}^{(\mu)} = \frac{2\pi}{|\vec{C}_h|} \mu$. Hence, the resulting wavefunction becomes:

$$\psi_{\mu,k_z}(\vec{r}) \propto \exp(ik_z z) \exp(ik_{\perp}^{(\mu)} \phi) u_{\mu,k_z}(\vec{r}), \quad (3.33)$$

in terms of the circumferential angle ϕ .

From Eqs. 3.30–3.33, the electric field aligned along z (the nanotube axis) implies that the transition matrix element is only non-zero when the circumferential parts cancel exactly:

$$\int \exp(i(k_{\perp}^{(\mu')} - k_{\perp}^{(\mu)})\phi) d\phi \neq 0 \quad \Rightarrow \quad \mu = \mu'. \quad (3.34)$$

This orthogonality condition for angular momentum eigenstates ensures that only $\Delta\mu = 0$ transitions are optically active under parallel polarization. For perpendicular polarization, transitions with $\Delta\mu \neq 0$ are symmetry-allowed but typically exhibit weaker oscillator strength.

Table 3.1: Time scale comparison for different optical transition mechanisms in SWCNTs.

Transition Type	Mechanism	Typical Timescale
Inter-subband	Ultrafast nonradiative relaxation between higher subbands via acoustic or optical phonon emission (e.g., $S_{22} \rightarrow S_{11}$)	~ 40 fs [151, 194]
Intra-subband	Carrier scattering within the same subband due to phonons or defects	-
Inter-tube	Rapid decay in nanotube bundles	~ 1 ps [88, 128, 216]
Exciton recombination	Radiative decay of bound excitons, typically at the S_{11} transition in semiconducting tubes	~ 110 ns [216, 213, 194]
Nonradiative recombination	Energy dissipation through phonons or defects, competing with radiative processes	~ 10 – 100 ps [216, 194]

By observing the allowed transitions from the valence band to the conduction band, semiconducting SWCNTs exhibit strong photoluminescence, predominantly from the S_{11} transition, following excitation at higher-energy states such as S_{22} . Upon such excitation, carriers undergo ultrafast intersubband relaxation to the S_{11} level, primarily through the emission of acoustic or optical phonons. This process typically occurs within 40 fs, facilitated by strong electron-phonon coupling and the 1D density of states characteristic of SWCNTs [151, 194]. After reaching the S_{11} level, carriers may experience further intraband scattering due to interactions with phonons or structural imperfections. In the case of bundled nanotube samples, additional inter-tube transitions can occur, whereby excitons or charge carriers transfer between adjacent tubes within roughly 1 ps [88, 128, 216].

Upon localization in the S_{11} state, strong Coulombic interactions between photoexcited electrons and holes give rise to tightly bound electron-hole pairs with binding energy about 300-500 meV, referred to as excitons, which can subsequently recombine through either radiative or nonradiative pathways [195, 142, 15]. Radiative recombination at S_{11} results in near-infrared photoluminescence, with lifetimes spanning 110 ns, influenced by nanotube chirality, dielectric environment, and exciton diffusion dynamics [130, 216, 213, 194]. Competing with this are nonradiative recombination pathways, including multi-phonon emission and trapping at defect sites, which typically occur over 10 ps to 100 ps and substantially diminish photoluminescence efficiency [216, 194]. A comprehensive understanding of these ultrafast carrier dynamics is essential for the development of efficient SWCNT-based optoelectronic and photonic devices (Table 3.1).

While the pure free-carrier model describes optical transitions as vertical excitations from the valence band to the conduction band, the excitonic model in semiconducting SWCNT provides a more comprehensive framework by accounting for the formation and dynamics of bound electron-hole pairs, or excitons, which govern the optical response.

Interestingly, excitons in SWCNT are often classified as Wannier-Mott excitons based on their spatial extent, which typically ranges from 10 to 100 Å. However, despite their relatively large size, they exhibit exceptionally large binding energies, on the order of several hundred meV, comparable to those of Frenkel excitons. As a result, SWCNT are described as hosting strongly bound Wannier excitons with delocalized wavefunctions.

Considering the degeneracy of the K and K' points in the graphene Brillouin zone (Fig. 3.6(b)), which gives rise to valley and spin degeneracies, semiconducting SWCNT exhibit a unique electronic structure characterized by fourfold degeneracy. This re-

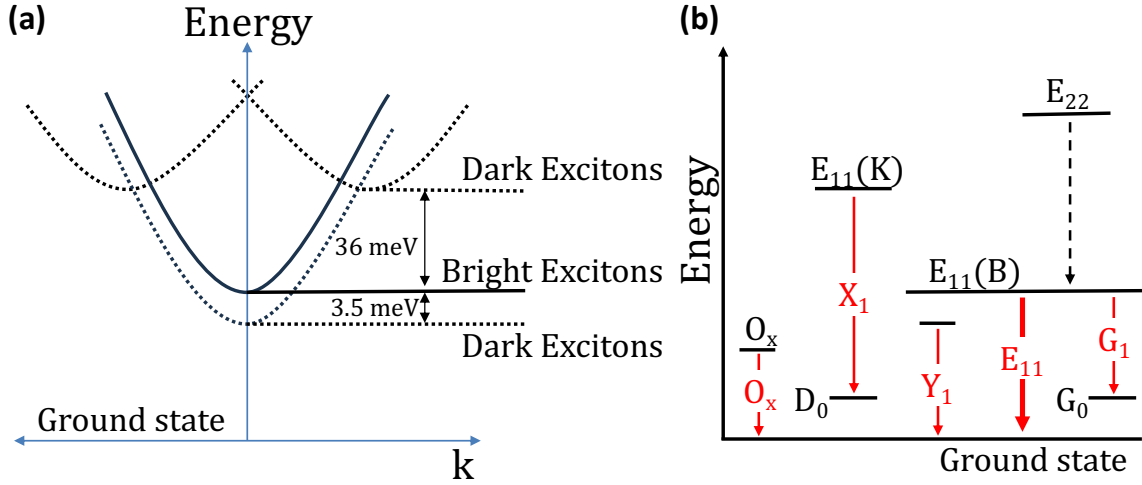


Figure 3.8: (a) Example of the excitonic band structure in a [SWCNT](#), where one excitonic state is optically active (bright), and the remaining are optically inactive (dark). The energy values shown correspond to the (6,5) chirality and are adapted from [105, 208, 160]. (b) Jablonski diagram illustrating the energy levels and optical transitions in a (6,5) [SWCNT](#), redrawn from [139].

sults in a total of four singlet and twelve triplet excitonic states [53], as illustrated in Fig. 3.8(a). Among these states, only one optical transition is symmetry-allowed, corresponding to the bright singlet exciton, as shown in Fig. 3.8(b) [139].

The dominant [PL](#) signal originates from the bright singlet exciton state with odd parity and zero center-of-mass momentum, denoted as $E_{11}(B)$ [213]. Energetically, the dark singlet exciton state with even parity, along with all triplet exciton states, lies below the bright $E_{11}(B)$ level. In contrast, another optically inactive state, $E_{11}(K)$, characterized by odd parity and finite center-of-mass momentum at the K-point, is positioned above $E_{11}(B)$. The primary radiative transition observed in semiconducting [SWCNT](#) is the E_{11} transition, which arises from the recombination of bright excitons in the $E_{11}(B)$ state. In addition to this strong and narrow emission peak, several weaker and red-shifted features, collectively referred to as photoluminescence sidebands (PSBs), are observed in the emission spectrum, particularly in well-characterized chiral species such as the (6,5) [SWCNT](#), as shown in Fig. 3.8(b) [139]. Each PSB has a distinct origin. The G_1 sideband arises from phonon-assisted recombination of the $E_{11}(B)$ exciton, mediated by the emission of a G_0 phonon [23]. The X_1 sideband results from the radiative decay

of the momentum-forbidden $E_{11}(K)$ exciton, which becomes optically allowed via the emission of a D_0 phonon [23, 208]. The Y_1 feature is believed to stem from extrinsic effects and exhibits variability across samples and individual nanotubes [111]. Additionally, the O_x transition, also observed in (6,5) SWCNTs under ambient conditions, displays synthesis-dependent behavior and is likely associated with unintended luminescent oxygen-related defects [76].

The optical properties of SWCNTs are not solely determined by their intrinsic electronic structure but are also highly sensitive to external environmental factors. Dielectric screening from the surrounding medium can significantly modify Coulomb interactions, leading to shifts in excitonic transition energies [174]. Furthermore, doping or charge transfer, induced by interactions with surfactants, polymers, or chemical adsorbates, can quench PL and alter absorption features due to changes in carrier concentration and exciton binding energies [32]. Structural strain and defects also play a crucial role by breaking symmetry, introducing mid-gap states, and enabling otherwise forbidden optical transitions. These perturbations often manifest as peak broadening or the emergence of new spectral features [21]. As such, understanding and controlling environmental effects are essential for tailoring the optical response of SWCNTs in practical optoelectronic applications.

Building upon these studies of SWCNT excitonic states, the PL from the (6,5) chirality is utilized as a platform to investigate light–matter interactions, serving as a medium to demonstrate lasing phenomena.

Chapter 4

Single-Walled Carbon Nanotubes in Cavity

Photoluminescence (PL) in SWCNTs has been extensively investigated since its first observation in liquid-phase dispersions in 2002 [168]. These dispersions enable facile optical characterization using commercially available spectroscopic techniques, allowing detailed investigation of excitonic transitions, optical selection rules, and chirality-dependent emission properties. Although such solution-based systems are valuable for fundamental studies, they are not directly compatible with solid-state optoelectronic device architectures. For practical applications, it is crucial to fabricate and characterize SWCNT thin films, which can serve as active layers in photonic and electronic devices.

However, photoluminescence efficiency in solid-state SWCNT films remains limited due to several intrinsic and extrinsic factors. The photoluminescence quantum yield (PLQY), defined as the ratio of photons emitted to photons absorbed, is intrinsically low in SWCNT. As reviewed in Chapter 3, this originates from the excitonic fine structure, where only one out of sixteen spin–valley exciton states is optically active, i.e., bright [213, 53]. Furthermore, extrinsic factors such as nanotube bundling, misalignment, structural defects, and environmental quenching exacerbate the suppression of radiative recombination [207, 41, 167, 127].

The first measured PLQY in SWCNTs was on the order of 0.1% in SDS, dispersed solutions [168], primarily limited by bundling, mixed chirality, and quenching mechanisms [154]. Subsequent advances in purification and dispersion, particularly density gradient ultracentrifugation (DGU) using sodium cholate (SC), significantly improved

emission efficiency by minimizing intertube interactions. Crochet *et al.* reported a five-fold increase in PLQY to 1.1% under these optimized conditions [41]. Further enhancement, up to 7%, was demonstrated by Lefebvre *et al.* using suspended individual SWCNT, which effectively eliminate environmental interactions [131]. Nevertheless, such configurations are not viable for scalable device fabrication, and typical PLQY values in solid films remain below 0.1% [222]. To further improve emission efficiency, various chemical functionalization strategies have been explored. These include the use of oxygen-excluding surfactants (~20%) [110], incorporation of reducing agents [95], hybridization with graphene quantum dots [183], oxygen doping [58], and the introduction of sp^3 defects to create emissive localized states [188]. Depending on the specific experimental conditions, the PLQY exhibited enhancements ranging from 2-fold to as much as 30-fold.

Another promising approach for enhancing SWCNT photoluminescence lies in photonic structure integration. Embedding SWCNT films into optical cavities can modify the local photonic density of states and enhance radiative recombination through the Purcell effect, while also improving light extraction efficiency. Cavity types studied include FP resonators, WGM, plasmonic cavities, and photonic crystals as shown in Fig. 2.7. Among these, FP microcavities offer a compelling combination of simplicity, planar architecture, and compatibility with scalable fabrication, making them especially promising for device applications. The following sections will focus on recent advances in implementing FP cavities to enhance SWCNT photoluminescence.

4.1 Strategies for Enhanced Photoluminescence Quantum Yield

The effectiveness of PL enhancement in SWCNT using FP cavities is strongly influenced by the reflectivity of the cavity mirrors. As discussed in Chapter 2, high reflectance is typically achieved using many pairs of DBR composed of alternating layers of materials with contrasting refractive indices. To this end, researchers have employed DBR structures to improve cavity performance and enhance PL intensity of SWCNTs.

A notable early study by Gaufrès *et al.* [74] demonstrated significant PL enhancement by spin-coating chirality-sorted SWCNTs onto a dielectric DBR composed of 10 alternating pairs of SiO_2 and Si_3N_4 . The SWCNTs were sorted using a selective polymer wrapping technique with poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO), yielding samples enriched in the semiconducting (8,7) species. The resulting PL from the sorted

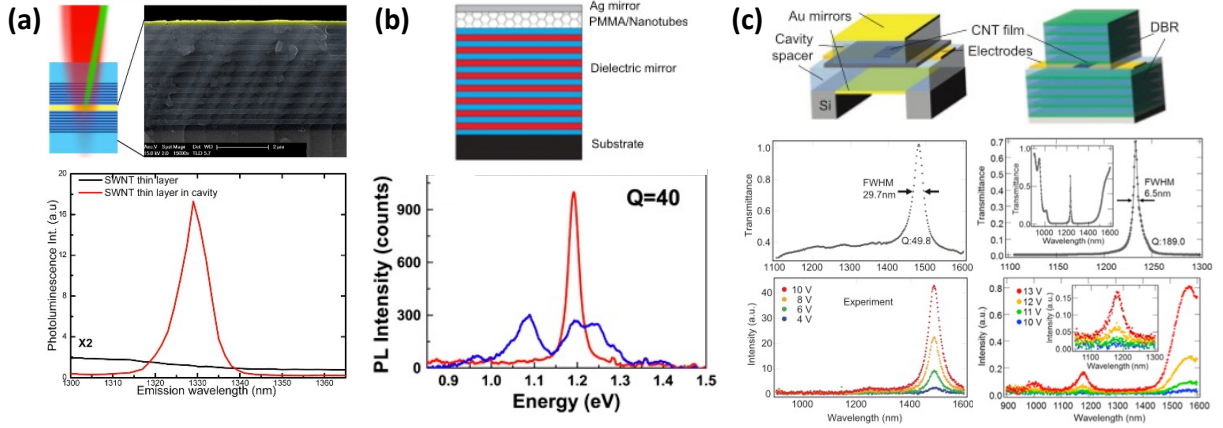


Figure 4.1: PL enhancement of SWCNT using FP cavities in selected experimental studies: (a) E. Gaufres *et al.* adapted from [74], (b) D. Legrand *et al.* reproduced from [132], and (c) M. Fujiwara *et al.* reprinted from [71]. Each configuration primarily employs DBR-based cavity designs to enhance PL intensity via optical resonance effects.

(8,7) nanotubes was enhanced by a factor of 30 compared to samples without the DBR, and by a factor of 180 compared to unsorted samples without a cavity. The structure and emission spectrum are shown in Fig. 4.1(a), with a reported cavity Q-factor of approximately 160.

In a different mirror configuration of hybrid DBR-metal mirror combination, Legrand *et al.* [132] used unsorted SWCNTs dispersed in PMMA and spin-coated them onto a 7.5-pair $\text{Ta}_2\text{O}_5/\text{SiO}_2$ DBR stack. In contrast to Gaufres *et al.*, the top mirror in this device was a 30 nm thick Ag layer deposited via thermal evaporation. While this hybrid dielectric-metal design resulted in a lower Q-factor of approximately 40, the PL intensity still increased by over threefold compared to the non-cavity control, as shown in Fig. 4.1(b).

Fujiwara *et al.* [71] further explored the effects of mirror material by directly comparing metal and dielectric cavities side-by-side, as illustrated in Fig. 4.1(c). In their study, electroluminescence (EL) was used to excite the SWCNTs. For the metal cavity, Au mirrors of 75 nm and 50 nm were used as the bottom and top reflectors, respectively. The SWCNT emitter layer was directly synthesized on the cavity spacer via CVD using patterned Co catalysts. In contrast, the dielectric DBR cavity employed 5-pair $\text{SiO}_2/\text{TiO}_2$ layers was fabricated by sputtering, and the SWCNT film was deposited between two DBRs via spin-coating of an SDS, dispersed solution. The DBR-based device produced roughly four times higher emission than the metal-mirror device, attributed

to its significantly higher **Q-factor** (189 versus 50).

These early investigations into cavity-enhanced **SWCNT** emission collectively mark the foundational development of **FP**-cavity-based **SWCNT** light-emitting devices. A consistent theme across these works is the use of dielectric mirrors, particularly **DBRs**, which provide higher reflectivity and enhancement of **Q-factor** and **PL** emission intensity than metallic counterparts. Hybrid cavities using a **DBR** bottom mirror and a metallic top mirror offer a practical fabrication route but generally result in lower **Q-factors**. Even in the best-performing dielectric cavities, the reported **Q-factors** remain modest (160–190), indicating room for further optical optimization. Another critical insight from these studies is the importance of **SWCNT** purification and chirality sorting. The presence of metallic nanotubes and bundles significantly degrades **PL** intensity. Therefore, high-purity, well-dispersed, and chirality-enriched **SWCNT** films are essential for maximizing cavity-coupled emission performance.

Early studies on **PL** enhancement in **SWCNT** films utilized **FP** resonators to amplify emission signals. These approaches built upon prior demonstrations of **PL** from individual **SWCNTs** in solution-phase dispersions [168] and isolated single-tube measurements [129]. While the implementation of **FP** cavities effectively increased **PL** intensity, the observed enhancements were limited to the weak light–matter coupling regime, without fundamentally altering the excitonic properties of **SWCNTs**. The following section explores a new generation of studies targeting the strong-coupling regime, where hybrid light–matter quasiparticles known as exciton-polaritons.

4.2 Single-walled Carbon Nanotube Exciton-Polaritons

As the field of exciton-polariton research continues to progress, the strong oscillator strength and large exciton binding energy of **SWCNTs** have made them promising gain media for exciton-polariton devices. In particular, extensive investigations have been conducted by the Zaumseil group, which has developed and refined selective polymer-sorting techniques for **SWCNTs** [82, 186]. Leveraging these methods, they have conducted a series of exciton-polariton experiments.

In 2016, Graf *et al.* [81] systematically studied exciton-polariton formation in **SWCNT** films embedded in **FP** cavities (Fig. 4.2(a)). They employed Au mirrors for both the top and bottom cavity reflectors and varied the film thickness of **PFO-BPy** sorted **SWCNTs**, yielding samples enriched in the (6,5) chirality. Angle-resolved reflectance and **PL** spectroscopy revealed two upper and lower polariton dispersion branchess, separated by a

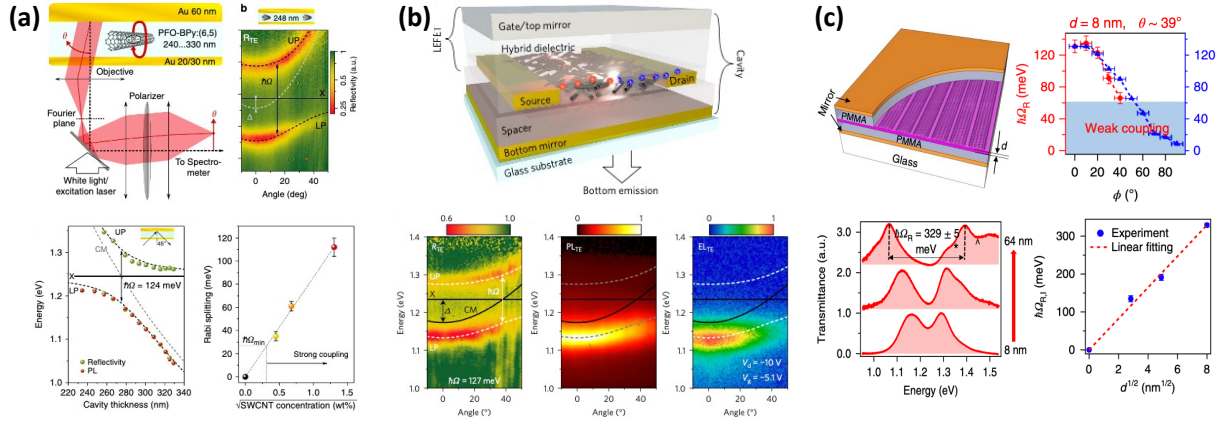


Figure 4.2: Exciton-polariton studies with SWCNT in FP cavities in selected experimental studies: (a) A. Graf *et al.* in 2016 adapted from [81], (b) A. Graf *et al.* in 2017 reproduced from [80], and (c) W. Gao *et al.* reprinted from [73].

large pronounced VRS. The splitting magnitude depended on both the cavity detuning values and the SWCNT film thickness, which was correlated with nanotube concentration.

A key result from this study was a linear relationship between VRS and the square root of SWCNT concentration, as shown in right bottom of Fig. 4.2(a). Building on this work, Graf *et al.* [80] further demonstrated EL in SWCNT-based exciton-polariton devices. By integrating electrodes into the microcavity structure, they compared PL and EL characteristics, confirming the persistence of polaritonic features under electrical excitation, as illustrated in Fig. 4.2(b).

Another notable contribution came from Gao *et al.* [73], who focused on the SWNT film quality. They employed a vacuum filtration method to fabricate densely packed, highly aligned SWCNT films, which were integrated into a metal microcavity. This alignment introduced strong polarization-dependent optical responses, leading to anisotropic VRS. Their system achieved Rabi splitting energies up to 329 meV, as shown in Fig. 4.2(c), demonstrating the strength of light-matter coupling in such systems.

There were two different sorting strategies to prepare SWNT films in these studies. Graf *et al.* used the selective polymer-wrapping method with PFO-BPy, which enabled high-purity semiconducting SWCNT films with strong PL and well-defined exciton-polariton dispersions observed in both PL and reflectance spectra. In contrast, Gao *et al.* used ATPE, a method discussed in a later chapter. However, their samples showed

little to no PL, likely due to residual metallic SWCNTs or excessive bundling from dense film packing, which quenches excitonic emission.

Interestingly, all three studies adopted simple metal mirrors with Au, Ag, or Al, rather than dielectric DBRs. The Q-factor in these metal-based cavities was typically around 23, significantly lower than what can be achieved with DBR-based cavities. Nevertheless, strong light-matter interactions were evident, with VRS energies typically exceeding 125 meV, and in some cases reaching up to 329 meV, underscoring the high oscillator strength of SWCNTs.

However, despite exhibiting strong light-matter interaction characterized by large Rabi splitting values, all CNT-cavity studies to date have remained in the linear regime under low excitation pump power. None of these studies have demonstrated exciton-polariton condensation or coherent lasing effects. We attribute this limitation partly to the low Q-factor of the metal-mirror cavities, which likely restricts the build-up of coherence necessary for such phenomena.

4.3 Endeavors in Resonator Architectures for Enhanced Emissions

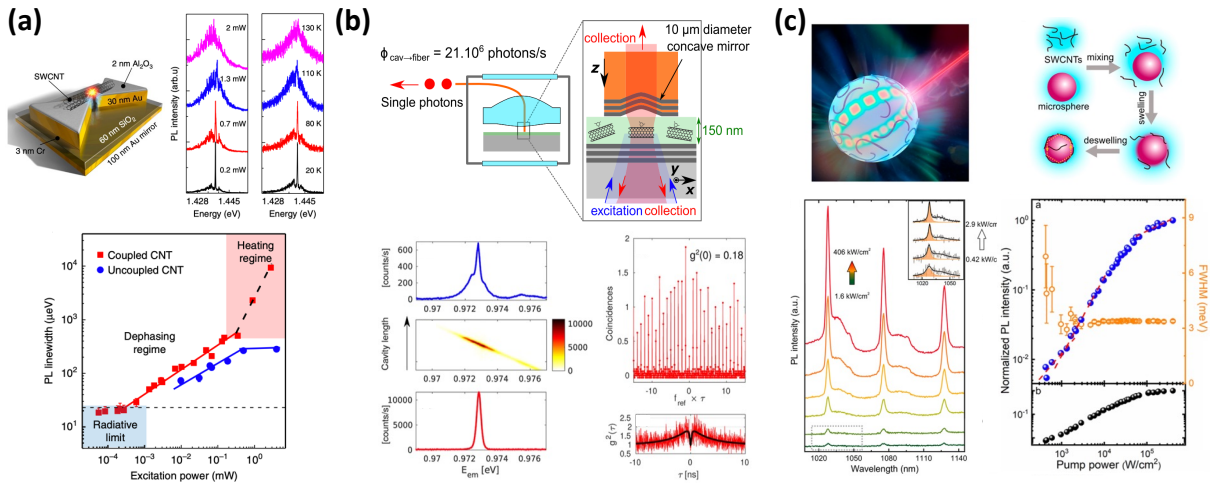


Figure 4.3: (a) SWCNTs on bowtie shape plasmonics cavity adapted from [138], (b) on fibered FP cavity reproduced from [26], (c) on sphere WGM reprinted from [31].

Efforts to enhance the PL intensity from SWCNTs have evolved beyond the optimization of material preparation to include the strategic integration of various optical resonator architectures. These resonators, including planar microcavities, dielectric DBR structures, photonic crystals, and plasmonic cavities, are employed to confine light spatially and spectrally, thereby strengthening light–matter interactions and improving emission efficiency. By tailoring the photonic environment, these structures can significantly increase the radiative recombination rate of excitons in SWCNTs via the Purcell effect, enabling brighter and more directional emission. Until the publication of a lasing demonstration in 2022 [31], previous studies had primarily focused on enhanced spontaneous emission (Purcell effect) and single-photon sources driven by the promise of SWCNTs as nanoscale quantum light sources rather than achieving true lasing action.

Luo *et al.* [138] fabricated bowtie-shaped plasmonic cavities composed of 30 nm thick Au with nanogaps ranging from 10 nm to 20 nm. To mitigate quenching effects commonly associated with direct metal contact, a thin dielectric spacer layer of Al₂O₃ was deposited on top of the cavity structure. Subsequently, laser vaporization-synthesized SWCNTs were deposited after chirality sorting via the PFO-BPy method, as illustrated in Fig. 4.3(a). The resulting array of cavity-coupled SWCNTs exhibited PL enhancement when compared to uncoupled reference samples. Notably, the emission displayed strong polarization dependence and single-photon emission characteristics, evidenced by a measured second-order correlation value of $g^{(2)}(0) \sim 0.3$ using a Hanbury Brown and Twiss interferometer. The coupled cavities achieved a maximum Purcell factor of 180, with an average value of 57. The quantum yield was also substantially improved, reaching enhancements of up to 62% (average 42%). However, despite these achievements, no lasing behavior was observed: the PL linewidth broadened with increasing pump power, indicating the absence of coherent stimulated emission.

A novel class of FP cavities utilizing optical fibers has also been explored [26]. In this configuration, DBR coatings were applied to the tips of optical fibers, which were then aligned above planar substrates that also contained DBR mirrors and cavity layers. The cavity length could be finely tuned by adjusting the gap between the fiber and the substrate, enabling precise control of the resonance wavelength to optimize PL output. This design yielded cavities with Q-factor values exceeding 10,000 and the Purcell factor as high as 30. Single-photon emission was demonstrated with a measured $g^{(2)}(0) \sim 0.18$ and an output photon rate of up to 20 MHz, as shown in Fig. 4.3(b).

In a related but distinct application, Chernysheva *et al.* [36] reviewed a saturable absorber-based ultrafast laser using SWCNTs integrated onto fiber systems. The device leveraged the ultrafast recovery time of SWCNTs (approximately 1 ps) to achieve mode-locking in the laser. Although this approach deviates from FP-based cavity lasers, the

fabrication method, especially the integration of SWCNT films onto fiber facets, serves as an important benchmark for future photonic devices.

The first experimental demonstration of lasing from SWCNTs was reported by Chen *et al.* in 2022 using a WGM resonator [31]. In this work, chirality-sorted SWCNTs (via PFO-BPy) were wrapped around silica microspheres of 5 μm diameter, forming high Q-factor resonators with values ranging from 139 to 1629. Optical pumping was performed using a pulsed laser with a 3.4 ps pulse width and 80 MHz repetition rate at 820 nm. The devices exhibited clear threshold behavior and a sharp spectral linewidth narrowing to approximately 3 meV, confirming the onset of lasing, as depicted in Fig. 4.3(c). While the first demonstration of lasing with SWCNTs represents a significant milestone, it is important to note that this achievement was not realized using SWCNT films, nor was it implemented within a scalable device architecture. As such, key challenges remain in translating this progress toward practical, large-area, and manufacturable carbon nanotube-based laser systems.

4.4 Motivation and Scope of the Research

Tables 4.1 and 4.2 summarize key studies on resonator-enhanced PL from SWCNTs, with particular emphasis on FP cavity structures. These studies can be broadly categorized into two phases based on the development of SWCNT purification techniques and cavity design methodologies.

In the initial phase, represented by the top three entries, unsorted or minimally purified SWCNTs were employed, as advanced sorting techniques were not yet widely available. During this period, DBR cavities were commonly used due to their high reflectivity compared to metal mirrors. These early FP cavities achieved Q-factors up to 189 and demonstrated significant PL enhancement [71]. However, detailed physical characterizations, such as Purcell factor or quantum yield measurements, were largely absent.

As SWCNT purification methods advanced, particularly with the adoption of polymer-wrapping techniques such as the well-known PFO-BPy method, chirality-sorted, semi-conducting SWCNTs (e.g., (6, 5) chirality) became accessible. These high-purity materials, with strong oscillator strengths, enabled exploration into exciton–polariton physics. In the next group of studies, polymer-wrapped SWCNTs were incorporated into optical cavities to investigate strong light–matter coupling [81, 80]. Notably, one study exploited vacuum filtration to create highly aligned SWCNT films, achieving a record-high VRS of 329 meV, although exciton–polariton condensation was not realized [73].

Table 4.1: Collection of resonator structures used in SWCNT studies.

Reference	SWCNT	Resonator	Gain media / Mirror
E. Gaufrés <i>et al.</i> [74]	(8,7) enriched	FP	PFO sorted SWCNT film 200 nm DBRs (SiO ₂ & Si ₃ N ₄)
D. Legrand <i>et al.</i> [132]	Mixed chirality	FP	SWCNT in PMMA 340 nm / Ag 30 nm & DBR (Ta ₂ O ₅ & SiO ₂)
M. Fujiwara <i>et al.</i> [71]	Mixed chirality	FP	CVD grown or spincoating / Both Au or both DBR
A. Graf <i>et al.</i> [81]	(6,5) enriched	FP	PFO-BPy sorted SWCNT film, Spincoating 240 - 330 nm / Both Au
A. Graf <i>et al.</i> [80]	(6,5) enriched	FP	PFO-BPy sorted SWCNT film, Spincoating 19 - 33 nm / Both Au
W. Gao <i>et al.</i> [73]	(6,5) enriched	FP	Vacuum filtrated aligned SWCNT, 8, 24, & 64 nm / Both Au or Al
Y. Luo <i>et al.</i> [138]	(5,4) or (6,4)	Plasmonic	PFO-BPy sorted SWCNT, single SWCNT on bowtie cavities
A. Borel <i>et al.</i> [26]	(7,5) enriched	Fibered-FP	PFO sorted SWCNT film / DBR (SiO ₂ & TiO ₂) on fiber tips
J. Chen <i>et al.</i> [31]	(6,5) enriched	WGM	PFO-BPy sorted & functionalized SWCNT / On 5 um microspheres

Beyond FP cavities, other resonator types have also been explored for PL enhancement. For instance, bowtie plasmonic structures have demonstrated high Purcell factors and quantum yields, but only PL enhancement, not lasing, has been reported [138]. Similarly, fiber-based FP cavities offer high Q-factors, but have not progressed beyond emission studies [26]. In contrast, microsphere-based WGM resonators have achieved room-temperature lasing from SWCNTs [31]. While their Q-factors are lower than 1000, they exhibit clear linewidth narrowing and pump-dependent behavior indicative of lasing.

Based on the unique optical properties of SWCNTs, specifically, their localized excitons with high oscillator strengths, NIR emission, and room-temperature tunability, and leveraging their optical coupling with scalable FP cavity structures achieving Q-factors exceeding 1000, these features present a promising route toward demonstrating lasing. Such systems hold strong potential for future applications in quantum photonic devices.

Table 4.2: Collection of resonator properties used in SWCNT studies.

Reference	Q-factor	Purcell factor	Quantum Yield	Rabi splitting
E. Gaufrés <i>et al.</i> [74]	~ 160	–	–	–
D. Legrand <i>et al.</i> [132]	40	–	–	–
M. Fujiwara <i>et al.</i> [71]	Au ~ 50 DBR 189	–	–	–
A. Graf <i>et al.</i> [81]	~23	–	–	≤ 112 meV
A. Graf <i>et al.</i> [80]	–	–	0.17%	≤ 127 meV
W. Gao <i>et al.</i> [73]		–	–	≤ 329 meV
Y. Luo <i>et al.</i> [138]	Expected 2-20	≤ 180 (Avg. 57)	$\leq 62\%$ (Avg. 42%)	–
A. Borel <i>et al.</i> [26]	≥ 10000	~30	~1%	–
J. Chen <i>et al.</i> [31]	Avg. 440 (139-1629)	–	–	–

Chapter 5

Single-Walled Carbon Nanotube Dispersion and Film

Based on the reviewed optical and electronic properties of SWCNTs, these materials hold great promise for future optoelectronic applications. However, a critical prerequisite for integrating SWCNTs into optoelectronic devices is the ability to prepare them with controlled morphology and high purity. Several key synthesis methods, CVD, arc discharge, and laser ablation, have been developed for the fabrication of SWCNTs, commonly yielding powder-like agglomerates. These techniques each offer specific advantages and limitations in terms of scalability, purity, and control over nanotube structure.

- **CVD:** This widely employed and industrially scalable method involves thermal decomposition of hydrocarbon gases (e.g., methane, acetylene, ethanol) at temperatures typically ranging from 600 °C to 1000 °C in the presence of dispersed metal nanoparticles supported on substrates such as SiO₂ or Al₂O₃. Carbon atoms dissolve into the catalyst particles and precipitate to form CNTs via either tip-growth or base-growth mechanisms, depending on catalyst–substrate interactions.
- **Arc Discharge:** In this high-temperature synthesis approach, a direct current arc between two graphite electrodes in an inert gas atmosphere (e.g., He or Ar) generates a carbon plasma that facilitates the formation of CNTs and fullerenes. This technique produces high-quality, highly crystalline CNTs, though with limited control over chirality, diameter distribution, and alignment [100].
- **Laser Ablation:** In this method, a high-power pulsed laser ablates a graphite target doped with transition metal catalysts at elevated temperatures. The vapor-

ized carbon condenses into CNTs upon cooling. Laser ablation yields high-purity SWCNT, but its complexity and cost render it less suitable for large-scale manufacturing [201].

Each synthesis strategy profoundly influences the morphology, defect density, alignment, and purity of CNTs, making a comprehensive understanding of the underlying growth mechanisms essential for tailoring their properties for applications in nanoelectronics, composites, energy storage, and biomedical systems. However, the as-synthesized CNT materials often present significant challenges, including strong van der Waals interactions that lead to nanotube bundling, a heterogeneous mixture of chiralities producing both metallic and semiconducting species, and the presence of undesirable by-products such as MWCNTs, amorphous carbon, structural defects, and residual catalyst nanoparticles (e.g., Fe, Ni, Co) [17, 103].

To transform synthesized materials into useful forms suitable for device fabrication, commonly thin films, purification and dispersion are essential processing steps. Raw (as-grown) SWCNTs must be dispersed in solution using surfactants, polymers, or organic solvents to separate individual tubes and remove contaminants [94]. This liquid-phase processing not only enables purification and sorting but also allows exfoliation of bundled tubes, thereby improving solubility and facilitating further integration into electronic, optoelectronic, bioimaging, and composite applications [145, 99, 47]. In this chapter, we provide a comprehensive overview of the process that spans from raw SWCNT materials to the fabrication of thin films and the subsequent characterization of their PL properties. The study of PL in the film state is particularly important for assessing the optical and optoelectronic behavior of SWCNTs at the device integration level. As emphasized in earlier discussions, the electronic and optical performance of SWCNT-based materials strongly depends on their structural purity and chirality uniformity. Therefore, the utilization of highly sorted SWCNTs is a prerequisite for achieving reproducible and high-performance device characteristics. To this end, we describe and critically compare two widely employed sorting methodologies: ATPE and polymer-wrapping-based sorting. The mechanisms, procedures, and practical considerations of each technique are presented, along with representative experimental results that illustrate their effectiveness in isolating specific chiralities. Following the sorting process, we outline the established protocols for fabricating uniform SWCNT films and investigate their PL behavior under various conditions. This analysis provides insight into the relationship between material processing, film morphology, and optical response.

5.1 Dispersion and Sorting Single-Walled Carbon Nanotubes

The initial step in enhancing the PL of SWCNTs involves preparing well-dispersed SWCNTs in solution by breaking down their aggregated structures. Aggregation occurs due to strong van der Waals interactions, which are attributed to the large surface contact arising from the high aspect ratio of the nanotubes, the highly delocalized π -electron cloud discussed previously, and the short inter-tube distances, typically ranging from 3.2 to 3.4 Å, which are sufficient to facilitate strong inter-tube attraction [54]. These inter-tube interactions lead to optical quenching effects, especially between semiconducting SWCNTs, or between semiconducting and metallic SWCNTs, resulting in non-radiative energy transfer that significantly suppresses PL.

To disaggregate SWCNTs, both *mechanical* and *chemical* methods, or a combination thereof, are employed [98, 229]. Among mechanical techniques, sonication is the most common and involves the application of high-frequency sound waves. Bath sonication is relatively gentle, while tip sonication delivers more intense mechanical energy directly to the samples. Shear mixing is another effective method, applying strong mechanical forces to disrupt nanotube bundles. It has been reported to be less damaging than sonication, often yielding longer nanotubes with higher PL efficiency [43, 82]. Homogenization, which relies on high-pressure differentials, operates similarly to shear mixing. Ball milling, on the other hand, involves grinding nanotubes with hard media in a rotating chamber, but it often causes significant structural damage and length reduction, making it less favorable for preserving SWCNT integrity.

Chemical dispersion methods aim to increase inter-tube spacing by modifying the nanotube surfaces. Surfactant-assisted dispersion is widely used, wherein surfactants coat the SWCNTs to lower surface tension and facilitate dispersion in aqueous media. Due to their inherent hydrophobicity, SWCNTs interact with the hydrophobic tail of amphiphilic surfactants, while the hydrophilic head promotes solubility in water [229]. Other chemical approaches include polymer wrapping and functionalization [141, 175, 12]. In polymer wrapping, polymers adsorb onto the SWCNT surfaces, enhancing both dispersion and stability. Functionalization can be covalent, such as the attachment of $-\text{COOH}$ or $-\text{OH}$ groups, or non-covalent, typically involving π - π stacking interactions with aromatic molecules, which better preserve the electronic structure of SWCNTs.

Nevertheless, neither mechanical nor chemical methods alone are sufficient to achieve stable and high-quality SWCNT dispersions. Mechanical methods may temporarily separate bundles, but without chemical stabilization, re-aggregation can occur. Con-

versely, chemical treatments require external forces to adequately expose the nanotube surfaces for modification. Therefore, an integrated approach combining both mechanical and chemical strategies is essential for producing dispersions with improved stability and PL properties.

Following dispersion, a purification step is typically employed to remove unwanted impurities such as damaged SWCNTs, amorphous carbon, carbon soot, catalyst residues, and even bundled SWCNTs that do not disperse well. The most common purification method involves ultracentrifugation, as these impurities tend to have higher densities and remain undispersed, forming pellets that can be easily separated after centrifugation.

To achieve high-purity CNT dispersions, we employ a two-step ultracentrifugation process in our laboratory:

- **Ultracentrifuge:** Optima XE-100, Beckman Coulter
- **Rotor:** Type 70.1 Ti (fixed-angle)
 - **Step 1:** 20,000 rpm for 1 hour 45 minutes
 - **Step 2:** 60,000 rpm for 45 minutes

This purification method is typically applied to surfactant-assisted dispersions of SWCNTs (e.g., CoMoCAT® or HiPco®) using surfactants such as SDS, DOC, or SC. After each ultracentrifugation step, the top supernatant, which contains well-dispersed CNTs, is carefully collected for either the next centrifugation step or for direct use in sample fabrication. The pellets, containing aggregated materials and other impurities, are discarded.

Once purified SWCNTs are prepared, the next step is the **sorting process**. In 2003, M. Zheng *et al.* first demonstrated DNA-based sorting, in which sequence-specific single-stranded DNA (ssDNA) wraps around SWCNTs based on their chiralities [236]. This pioneering work opened a pathway for sorting SWCNTs without deforming their structure, although the method is labor-intensive, expensive, and has limited scalability.

Following this demonstration, tremendous efforts have been made to develop alternative sorting methods, including:

- Selective covalent functionalization [196]
- Dielectrophoresis [124]

- Density gradient ultracentrifugation (DGU) [18]
- Polymer wrapping [164]
- Gel chromatography [199]
- ATPE [64]

Each method has its own advantages and disadvantages. Among them, ATPE and polymer wrapping using PFO-BPy are chosen for our device fabrication due to their economic feasibility and scalability for future development.

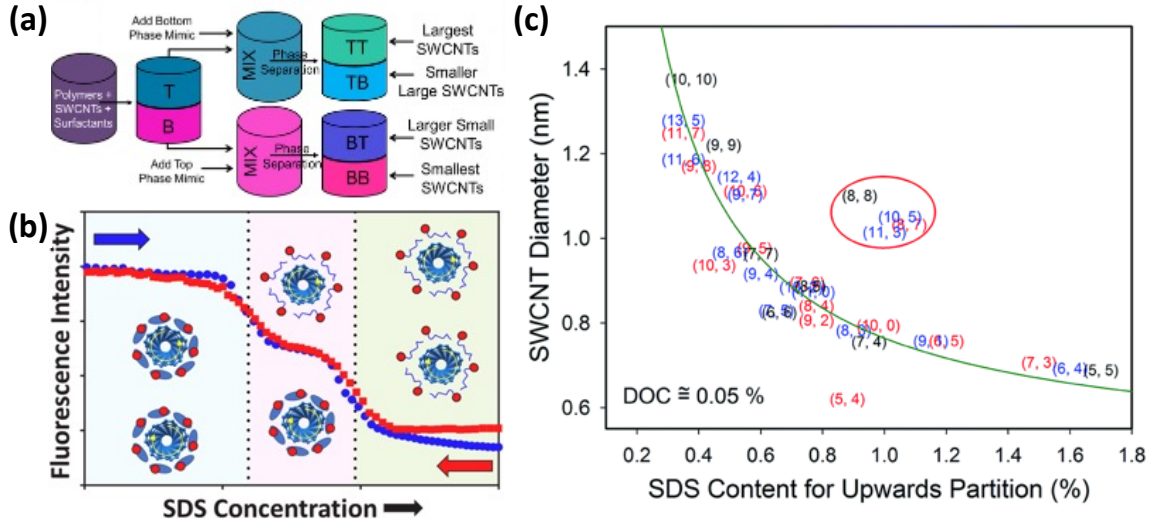


Figure 5.1: (a) Schematic illustration of the ATPE process adapted from [63], (b) Illustration of surfactant wrapping behavior in a two-surfactant system, showing how wrapping varies with changes in surfactant concentration reproduced from [193], (c) Diameter-dependent separation of SWCNTs as a function of SDS concentration at a fixed DOC concentration of 0.05% reprinted from [62].

5.1.1 Aqueous Two Phase Extraction (ATPE)

We first explored the ATPE method to extract single-chirality or, at minimum, highly enriched semiconducting SWCNT dispersions (with purity $\geq 99\%$). The underlying

mechanism of this process leverages the phase separation properties of polymer mixtures, a phenomenon first reported in 1958 by Albertsson [11]. A commonly used combination for phase separation is polyethylene glycol (PEG) and dextran (DX). When the concentrations of both polymers exceed their critical thresholds, the mixture spontaneously separates into two immiscible aqueous phases, despite appearing initially homogeneous. While this separation process naturally occurs over time, it can be significantly accelerated by low-speed centrifugation (e.g., 1500 rpm for several minutes).

This fundamental behavior forms the basis of the ATPE process, which is schematically illustrated in Fig. 5.1(a). Once purified SWCNTs with mixed chiralities are prepared, they are dispersed in a solution containing PEG, DX, and surfactants such as SDS and DOC. Due to their hydrophobicity nature, these surfactants preferentially partition into different phases: DOC tends to migrate into the DX-rich bottom phase due to its more hydrophobic character, whereas SDS favors the PEG-rich top phase. Consequently, SWCNTs are distributed between the two phases based on their interactions with these surfactants.

Through iterative processing, the initially mixed-chirality dispersion can be progressively refined into a single-chirality population. The sorting resolution is influenced by the differing affinities of surfactants for SWCNTs of various diameters. Notably, SDS, which has a longer alkyl chain than DOC, preferentially wraps around larger-diameter SWCNTs. As shown in Fig. 5.1(b), the wrapping behavior is highly sensitive to the concentrations of SDS and DOC, which results in diameter-selective separation. This relationship is further illustrated in Fig. 5.1(c), where a plot of sorted chiralities is shown as a function of SDS concentration at a fixed DOC concentration of 0.05% (w/v). A critical consideration throughout this process is the need to maintain precise concentration control, as the ATPE mechanism is extremely sensitive to variations in component ratios. (*All surfactant and polymer concentrations mentioned herein refer to mass/volume percentages (% w/v), where, for example, 1% (w/v) corresponds to 1 g of solute dissolved in 100 mL of solvent.) It should be noted that the above discussion pertains to diameter-based sorting. For electronic type separation, specifically, the differentiation of metallic from semiconducting SWCNTs, a redox-based modification of the ATPE process is required [62]. To further improve sorting precision, the use of *mimics*, mixtures of polymers and surfactants formulated to achieve exact concentration ratios, is recommended. Additionally, a polymer exchange step should be performed after sorting and prior to employing the sorted SWCNT dispersion in subsequent fabrication steps. Comprehensive details of the ATPE process, including theoretical background and experimental protocols, are provided in Appendix A.

Figure 5.2 and Figure 5.3 present the results of diameter-based ATPE sorting using

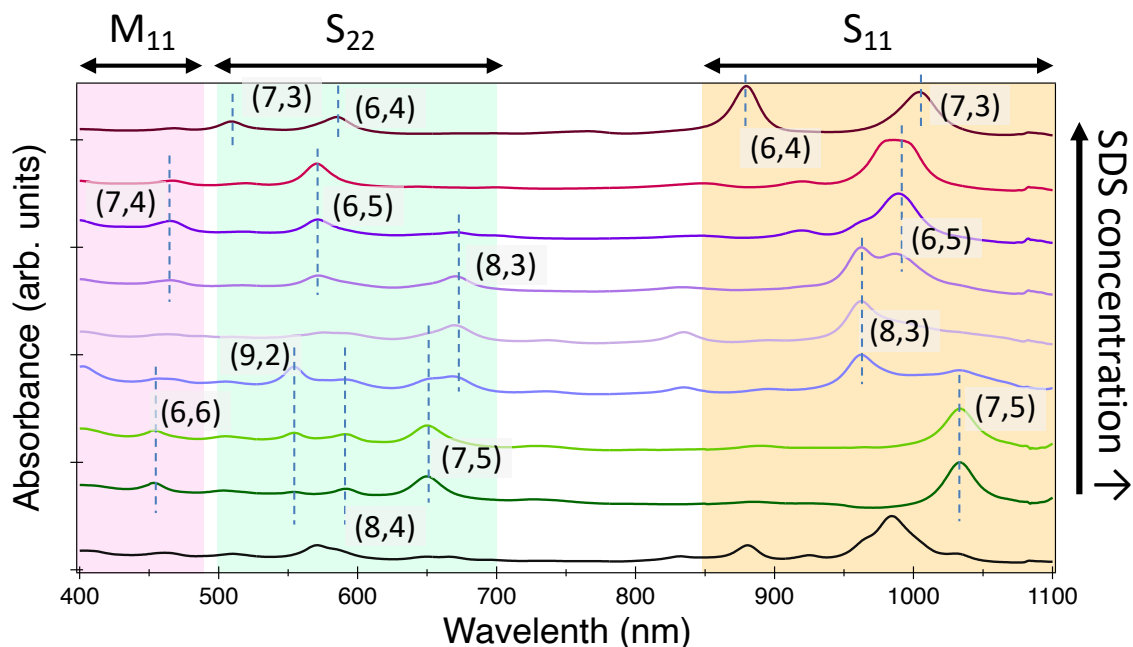


Figure 5.2: Representative absorbance spectra obtained from diameter-based ATPE sorting, measured using UV-Vis spectroscopy.

SG65i as the starting material. SG65i is a commercial SWCNT product manufactured by CHASM®, synthesized via the CoMoCAT® process, which is known for its high selectivity toward the (6,5) chirality. The “i” in SG65i indicates an improved version of the original SG65 product, offering higher purity and a greater proportion of semiconducting nanotubes. Specifically, SG65i contains approximately 95% semiconducting SWCNTs, with around 41% corresponding to the (6,5) chirality, while the remainder consists of other semiconducting and minor metallic chiralities.

Prior to sorting, a two-step ultracentrifugation purification protocol was applied to remove impurities and bundled nanotubes, resulting in a high-purity SWCNT dispersion in an aqueous solution containing 1.6% (w/v) DOC. For the ATPE sorting process, this dispersion was subsequently diluted to a final DOC concentration of 0.04% (w/v). Under these conditions, DOC molecules uniformly wrap SWCNTs of all chiralities, providing a stable and homogeneous suspension.

The fundamental strategy of diameter-based sorting via ATPE relies on the gradual addition of SDS at varying concentrations. Owing to its surfactant characteristics and higher affinity for larger-diameter nanotubes, SDS is capable of partially displacing

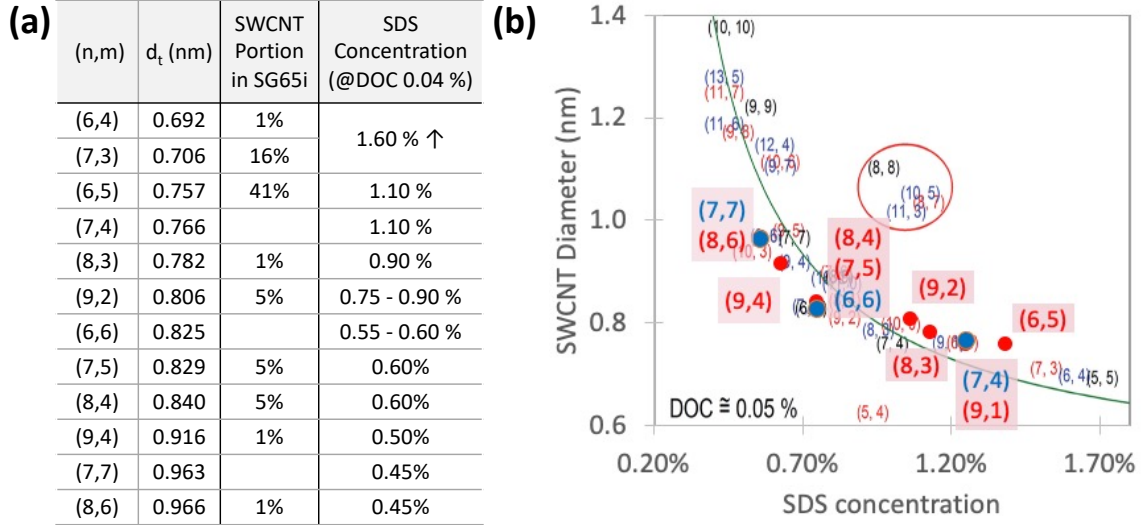


Figure 5.3: (a) Summary table showing the corresponding chiralities, diameters, relative SWCNT abundance in SG65i, and the optimal SDS concentrations at a fixed DOC concentration of 0.04% (w/v), (b) Comparison of the present diameter-based sorting results with the chirality–surfactant concentration map reported by Fagan *et al.* in Fig. 5.1(c) modified from [62].

DOC from the nanotube surface. This displacement modulates the interfacial interactions between SWCNTs and the surrounding polymer phases. As a result, chiralities preferentially partition into either the top PEG-rich or the bottom DX-rich phase depending on the nanotube–surfactant complex formed. This enables selective extraction of specific diameters based on the surfactant composition. As shown in Fig. 5.2, different SDS concentrations yield dispersions enriched with different chiralities, following a trend of descending nanotube diameter with increasing SDS concentration. DOC maintains a baseline wrapping across all chiralities, while SDS selectively modifies the micelle structure. This behavior is consistent with the surfactant diameter selectivity described in Fig. 5.1(b).

The absorbance spectra shown in Fig. 5.2 exhibit features arising from the van Hove singularities, notably the S_{11} transitions (yellow), S_{22} transitions (light green), and M_{11} transitions (pink), which correspond to semiconducting and metallic SWCNTs, respectively. The spectra are presented as waterfall plots, normalized for comparison. The bottom spectrum corresponds to the initial dispersion containing the full range of chiralities. As the sorting proceeds, SWCNTs with progressively smaller diameters are en-

riched at higher SDS concentrations, with the topmost spectra indicating the smallest diameter tubes.

Figure 5.3(a) summarizes key information, including chirality (n, m) indices, calculated diameters, the relative abundance of each chirality in SG65i (as specified by the distributor, Sigma-Aldrich, Product No. 773735), and the corresponding SDS concentration used to enrich each chirality under fixed DOC conditions (0.04% w/v). These optimized SDS concentrations were determined empirically from absorbance measurements after each sorting step. Finally, Fig. 5.3(b) maps the experimentally obtained chirality–SDS concentration relationships onto the chirality sorting trends reported by Fagan *et al.* [62]. While the experimental conditions differ slightly, most notably the DOC concentration, which was 0.04% (w/v) in this work versus approximately 0.05% in Fagan’s study, the data were adjusted accordingly to enable meaningful comparison. Despite these differences, the sorting trend is qualitatively consistent. It should be noted that ATPE separation is highly sensitive to environmental factors such as temperature, which may also contribute to minor discrepancies in chirality partitioning.

These results establish a foundational ATPE sorting recipe for our system. By tuning the SDS concentration with fixed DOC background, specific SWCNT chiralities can be selectively extracted with high reproducibility.

5.1.2 Polymer-Wrapping based Sorting Method

Although the ATPE sorting method is advantageous due to its economical and straightforward process, it is highly sensitive to environmental temperature fluctuations, and its selectivity is often insufficient for optoelectronic applications, as achieving high semiconducting purity remains challenging. In terms of both purity and process simplification, conjugated polymer-based sorting methods are generally preferred. Among these, PFO-BPy is well-known and was selected for application in this study.

PFO-BPy is a conjugated copolymer originally developed for optoelectronic and nanomaterial applications. Its molecular structure combines fluorene units, recognized for their photoluminescent properties, with bipyridine moieties (Fig. 5.4(a)) that can coordinate with metal ions, providing functionalization capabilities. In the context of SWCNT sorting, the alternating copolymer backbone of PFO-BPy promotes strong π - π interactions with specific SWCNT chiralities, particularly the (6,5) species synthesized by CoMoCAT®. PFO-BPy was developed from PFO, which exhibits high affinity for small-diameter SWCNTs and selectively disperses certain chiralities (e.g., ~79% enriched (7,5)). Building upon this, Ozawa *et al.* [171] reported that a fluorene-based

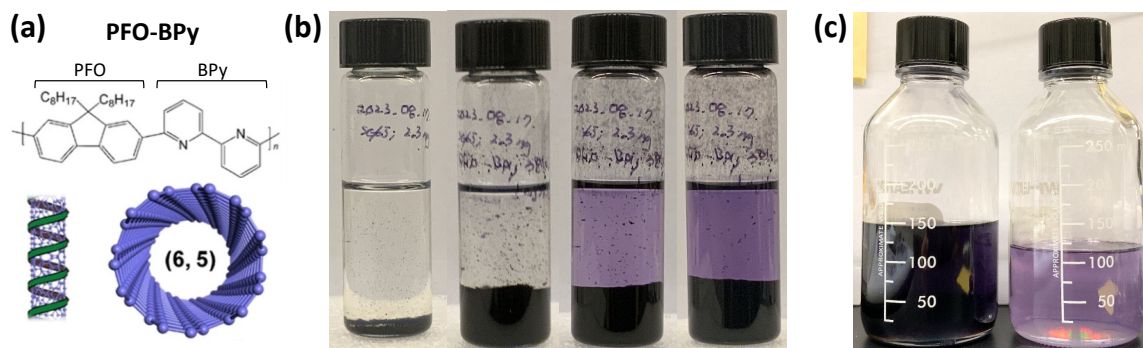


Figure 5.4: (a) Chemical structure of **PFO-BPy** and schematic representation of a (6,5) **SWCNT**, the most selectively extracted chirality when using CoMoCAT-produced material with **PFO-BPy** adapted from [137]. (b) Representative photograph showing sequential extractions during **PFO-BPy** sorting, using 14.7 mL glass vials, and (c) Final collection of sorted **SWCNT** dispersions stored in 250 mL glass bottles.

copolymer incorporating bipyridine units can achieve even higher selectivity (~96% enriched (6,5)) without metallic nanotube contamination. This enhanced selectivity is attributed to the polymer's ability to conform to the nanotube surface, stabilizing individual tubes in solution and facilitating effective separation from heterogeneous mixtures.

Selective sorting with **PFO-BPy** begins by dispersing the polymer in toluene. This dispersion is temperature-dependent, with an optimal temperature of 50 °C identified for maximizing polymer solubility and dispersion quality [171]. The polymer concentration was optimized to 1 mg/mL (1 mg **PFO-BPy** per 1 mL toluene) after testing a range from 0.5 to 9 mg/mL, balancing efficacy and economy. Large volumes of **PFO-BPy** solution are prepared in 500 mL glass bottles for use in sorting. For sorting, 10 mL of the dispersed **PFO-BPy** solution and 2.5 mg to 4 mg of **SWCNT** raw material are combined in a 14.7 mL vial. Mechanical processing is required to de-bundle the nanotubes, with tip sonication preferred for its efficiency and time-saving advantages over bath sonication and shear mixing. Temperature control is critical; therefore, the vial is immersed in a cooled water bath maintained at approximately 20 °C to 23 °C during sonication. Tip sonication is applied continuously at 50% amplitude for one hour using a Q125 sonicator (QSONICA). Following sonication, the sample is centrifuged at 1500 rpm for 3 minutes using an ST8 benchtop centrifuge (ThermoFisher).

Representative results are shown in Fig. 5.4(b). The leftmost vial depicts the mixture immediately after combining **PFO-BPy** and **SWCNT**s; the subsequent vial shows

the dispersion after sonication and centrifugation. Initial sonication typically does not fully de-bundle the **SWCNTs**, resulting in a clear top phase with residual black particles, assumed to be bundles. The supernatant (top phase) is carefully extracted, diluted with **PFO-BPy** solution to 10 mL, and the sonication-centrifugation cycle is repeated multiple times. Subsequent extracts show increasing enrichment and dispersion quality, with the top phase acquiring a characteristic purple color indicative of (6,5) **SWCNT** enrichment. These top-phase solutions are collected in a 500 mL glass bottle, as depicted in Fig. 5.4(c).

The centrifugation step removes unwrapped nanotubes and impurities, which sediment at the bottom of the vial. Despite this, some residual particles remain suspended in the top phase and can be co-transferred during collection, often corresponding to black particles of (7,5) or (6,4) chirality. To further purify the dispersion, an ultracentrifugation step is employed using a swing-bucket rotor (SW41) at 40,000 rpm for 3 hours in an Optima XE-100 ultracentrifuge (Beckman Coulter). This results in a high-purity, (6,5)-dominant semiconducting **SWCNT** dispersion.

Summary of the **PFO-BPy** Sorting Procedure:

- Bath sonicator: temperature controlled
- Tip sonicator: Q125 (QSONICA)
- Tip diameter: 1/8 inch, suitable for volumes up to 15 mL
- Benchtop centrifuge: ST8 (ThermoFisher)
- Ultracentrifuge: Optima XE-100 (Beckman Coulter)
- Rotor: SW41 swing bucket
- Sorting protocol:
 1. Disperse **PFO-BPy** in toluene at 1 mg/mL concentration; prepare large volumes in 500 mL glass bottles.
 2. Combine 10 mL of **PFO-BPy** solution with 2.5–4 mg of **SWCNT** raw material (SG65i) in a 14.7 mL vial.
 3. Perform tip sonication at 50% amplitude continuously for 1 hour under temperature control (20 °C).
 4. Centrifuge the sample at 1500 rpm for 3 minutes.

5. Extract the top phase, filter out black particles, and collect in a 500 mL glass bottle.
6. Replenish the vial to 10 mL with **PFO-BPy** solution and repeat steps 3–5 multiple times.
7. Ultracentrifuge the collected solution at 40,000 rpm for 3 hours using the SW41 rotor.
8. Collect the purified (6,5)-enriched dispersion in a new 500 mL glass bottle.



Figure 5.5: (a) A set of **PFO-BPy** samples with different molecular weights used for dispersion experiments from 33k to 135k g/mol, (b) Resulting dispersions after centrifugation using **PFO-BPy** samples with molecular weights of 33k, 38k, 40k, and 45k g/mol, respectively.

There are important considerations when purchasing **PFO-BPy** from American Dye Source, Inc., and when optimizing the number of extraction cycles to obtain a highly pure (6,5) dispersion.

The first consideration is the appropriate molecular weight of **PFO-BPy**. This conjugated polymer consists of repeated units of PFO(fluorene) and BPy (bipyridine), and the degree of polymerization critically influences its properties. The product ADS153UV, available from American Dye Source, Inc., is offered with a molecular weight range from approximately 10k to 150k g/mol. However, the exact molecular weight distribution is not precisely specified and varies within this range. In our study, we purchased **PFO-BPy** samples with molecular weights of 33k, 38k, 40k, 44k, 45k, and 135k g/mol (Fig. 5.5(a)).

The molecular weight of a single **PFO-BPy** repeat unit can be estimated as follows. The polymer chain comprises two segments: the PFO side, consisting of a fluorene

unit ($C_{13}H_{10}$) with two octyl side chains (C_8H_{17}), and the BPy side, a bipyridine unit ($C_{10}H_8N_2$). Their approximate molecular weights are:

- PFO side = Fluorene + 2 × Octyl ≈ 392 g/mol
 - Fluorene ($C_{13}H_{10}$) ≈ 166 g/mol
 - Octyl (C_8H_{17}) ≈ 113 g/mol
- BPy side = Bipyridine ($C_{10}H_8N_2$) ≈ 156 g/mol
- Total per repeat unit (PFO + BPy) ≈ 548 g/mol

Based on these values, the approximate degree of polymerization for each purchased sample is: 60.2 (33k), 69.3 (38k), 73.0 (40k), 80.3 (44k), 82.1 (45k), and 246.3 (135k).

We tested all six samples and identified an optimal molecular weight range for SWCNT sorting. It is well known that polymers with very high molecular weights are not suitable for this application. Specifically, longer polymer chains are less flexible due to chain entanglement and internal interactions, which hinders their ability to conform to the curved surfaces of SWCNTs. Furthermore, high molecular weight polymers experience steric hindrance that prevents close alignment with the nanotube surface. They also diffuse more slowly in solution, reducing their adsorption efficiency during dispersion. In addition, such polymers tend to aggregate or form gels in solvents, which impairs dispersion and can cause precipitation, leaving nanotubes undispersed. Their relatively low solubility in common solvents further restricts their interaction with SWCNTs. For these reasons, the 135k PFO-BPy sample disperses well in toluene but does not effectively wrap SWCNTs, resulting in no sorted dispersions.

Among the other samples, comparisons between 33k and 45k molecular weight PFO-BPy dispersions are shown in Fig. 5.5(b), which includes 33k, 38k, 40k, and 45k samples. The sample with 45k molecular weight exhibits a noticeably darker color compared to the others, indicating the presence of a broader range of SWCNT chiralities in the dispersion.

Two extinction peaks corresponding to the (6,4) and (7,5) chiralities are observed in the UV-vis absorbance spectrum of the 45k g/mol sample, which are absent in the spectra of lower molecular weight cases (Fig. 5.6). This spectral difference correlates with the visual observation shown in Fig. 5.5(b), where the 45k g/mol dispersion appears noticeably darker than the others. While the typical chirality purity of PFO-BPy

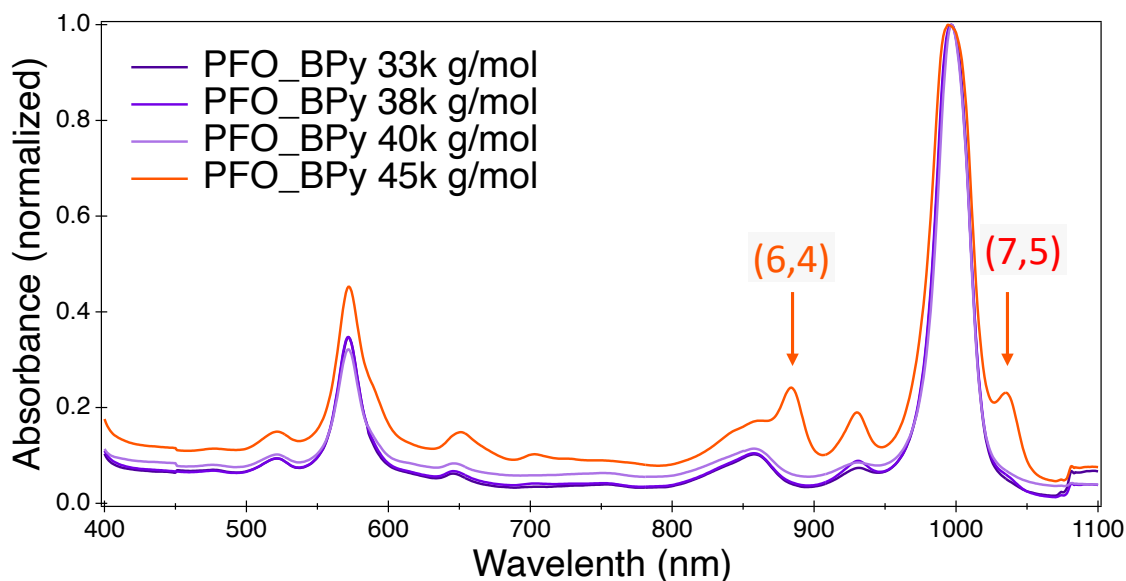


Figure 5.6: UV-vis absorbance spectra of PFO-BPy dispersions with molecular weights of 33k, 38k, 40k, and 45k g/mol, highlighting distinct spectral differences in the 45k g/mol sample.

for CoMoCAT®-derived SWCNTs is reported to be approximately 96%, indicating minimal presence of non-(6,5) chiralities [171], the 45k g/mol case exhibits reduced (6,5) purity. The underlying reason for this deviation remains unclear and requires further research.

The purity of chirality-sorted SWCNT dispersions using PFO-BPy is not solely determined by the polymer's molecular weight, but the number of extraction cycles also plays a significant role. In this study, up to the 11th extraction was performed on a dispersion sample using PFO-BPy with a molecular weight of 38k g/mol. The optical appearance of the dispersions gradually changed with each successive extraction, with later-stage samples exhibiting a deeper coloration that visually resembled the dispersion obtained using the 45k g/mol polymer, as shown in Fig. 5.5(b). To gain quantitative insight into this visual observation, UV-vis absorbance spectroscopy was employed. As illustrated in Fig. 5.7, the absorption spectra revealed a noticeable emergence and growth of non-target chiralities, specifically the (6,4) and (7,5) species, beginning from the 6th extraction. These features became increasingly pronounced in subsequent extractions, with the 11th sample clearly exhibiting distinct peaks corresponding to these undesired chiralities.

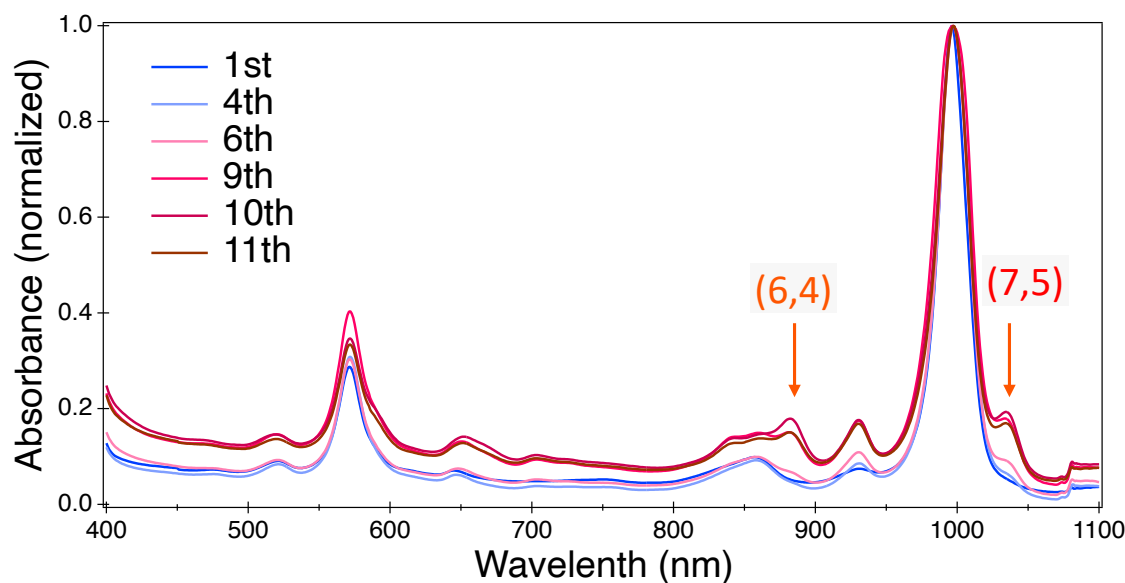


Figure 5.7: UV-vis absorbance spectra of **PFO-BPy** dispersions using the 38k g/mol sample across multiple extraction cycles, up to the 11th time.

This trend suggests a diminishing selectivity of the sorting process as the number of extractions increases, likely due to the gradual depletion of **PFO-BPy** chains with high affinity for the (6,5) chirality or changes in the dispersion environment that favor co-dispersion of other chiralities. These findings highlight the necessity of optimizing both the molecular weight and the number of extraction cycles to maintain high chirality purity in polymer-assisted **SWCNT** sorting.

As previously noted, the initially collected **PFO-BPy**, sorted **SWCNT** dispersion, prior to ultracentrifugation—contains notable contributions from (6,4) and (7,5) chiralities, as shown in Fig. 5.4(c)-left. Following the ultracentrifugation step described in the **PFO-BPy** sorting procedure, the resulting dispersion becomes significantly enriched in the (6,5) chirality, as evident in Fig. 5.8. Although the pre-ultracentrifugation dispersion appears optically clear and free of visible black particles, especially after filtration during phase separation, some non-(6,5) chiralities persist in the supernatant. Over time, typically beyond 24 hours, these undesired species aggregate and become visible as black precipitates due to polymer desorption. During ultracentrifugation, these aggregates sediment and form dense pellets at the bottom of the centrifuge tubes, resulting in a highly purified, (6,5)-dominant, deep-purple dispersion. This final product is well-suited for subsequent thin-film fabrication and optoelectronic device applica-

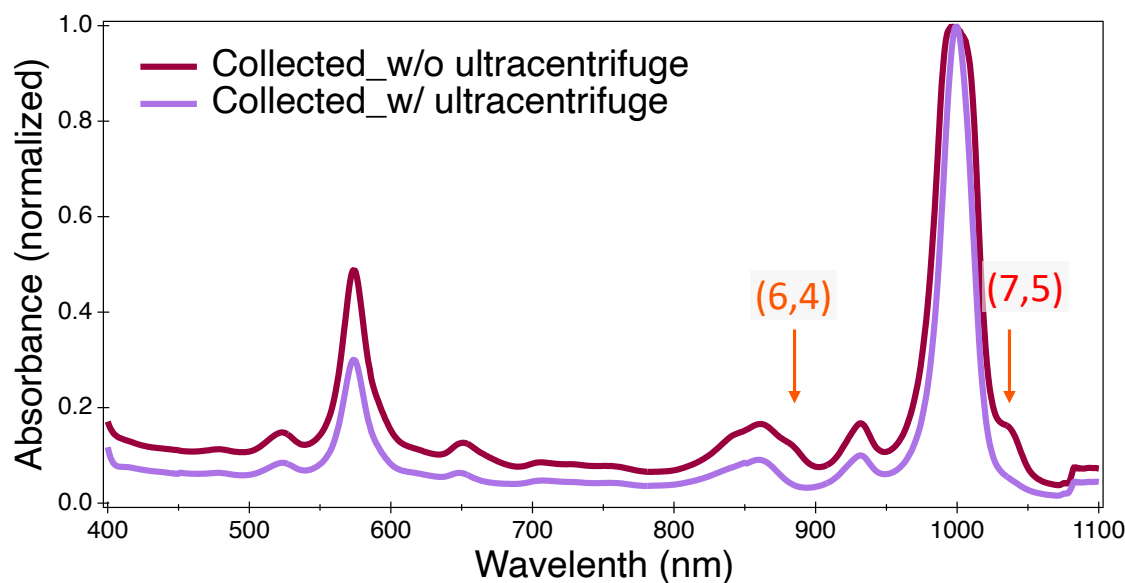


Figure 5.8: UV-vis absorbance spectra of PFO-BPy-sorted SWCNT dispersions before (left) and after (right) ultracentrifugation, corresponding to the samples shown in Fig. 5.4(c). The spectra highlight the improvement in dispersion purity achieved through the ultracentrifugation process.

tions.

5.2 Single-Walled Carbon Nanotubes Concentration in PFO-BPy solution

Before proceeding to SWCNT film fabrication, it is essential to establish a reliable method for estimating the nanotube concentration. UV-vis spectroscopy offers a non-destructive means of evaluating concentration based on absorbance spectra. When calibrated with TGA data, this method enables accurate concentration predictions from absorbance peak intensities.

Previous studies have demonstrated that PFO-BPy dispersed in toluene exhibits high selectivity toward the (6,5) chirality of SWCNTs, particularly when derived from CoMoCAT® materials. The resulting dispersions are highly enriched in semiconducting nanotubes. In such dispersions, UV-vis spectra consistently show pronounced (6,5)

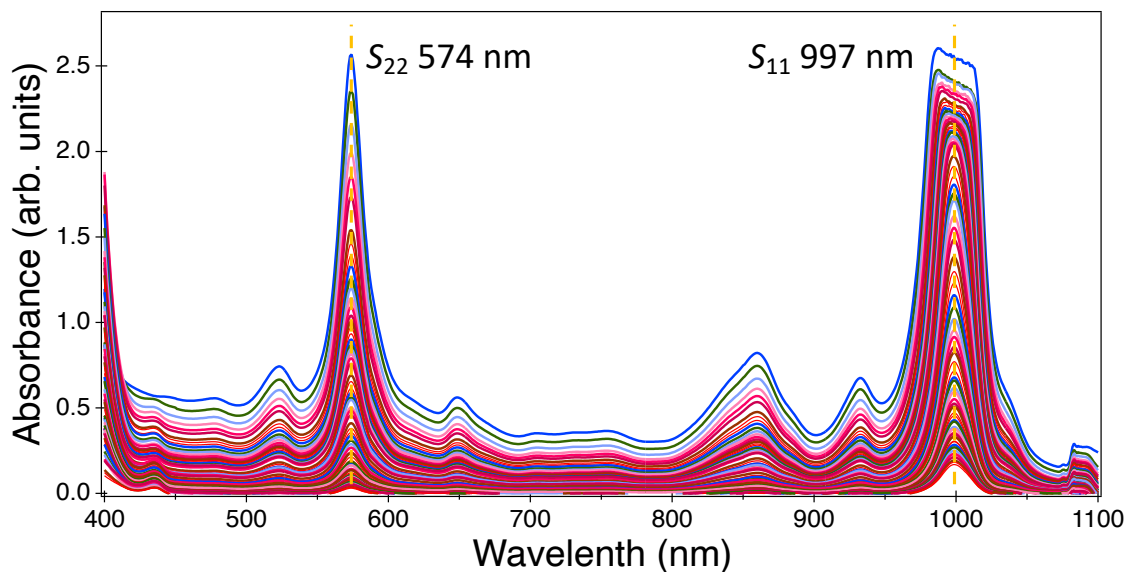


Figure 5.9: UV-vis absorbance spectra of **SWCNT** dispersions at varying concentrations, illustrating the trends in S_{11} and S_{22} absorbance peaks.

features, with S_{11} and S_{22} optical transitions centered at 997 nm and 574 nm, respectively.

To investigate the relationship between concentration and absorbance, a set of 72 samples with varying **SWCNT** concentrations was prepared. These were obtained by diluting an initially concentrated **PFO-BPy/SWCNT** dispersion with toluene. The corresponding UV-vis absorbance spectra are presented in Fig. 5.9. The S_{22} peak remains clearly visible across all concentrations and exhibits a **full width half maximum (FWHM)** of approximately 28 nm, as determined by Lorentzian fitting. In contrast, the S_{11} peak displays distortion at higher concentrations, particularly in samples with elevated absorbance, which will be discussed in a later section.

Based on the UV-vis absorbance measurements, the S_{11} and S_{22} peak intensities were analyzed as a function of the **SWCNT** concentration. For consistency and clarity, the concentrations were normalized to the maximum value and plotted against the corresponding absorbance peak intensities, as shown in Fig. 5.10. As previously observed in Fig. 5.9, the S_{11} peak shape becomes distorted at higher concentrations, a trend that is clearly reflected in its deviation from linearity above a relative concentration of 17%.

In contrast, the S_{22} peak maintains a linear relationship throughout the entire con-

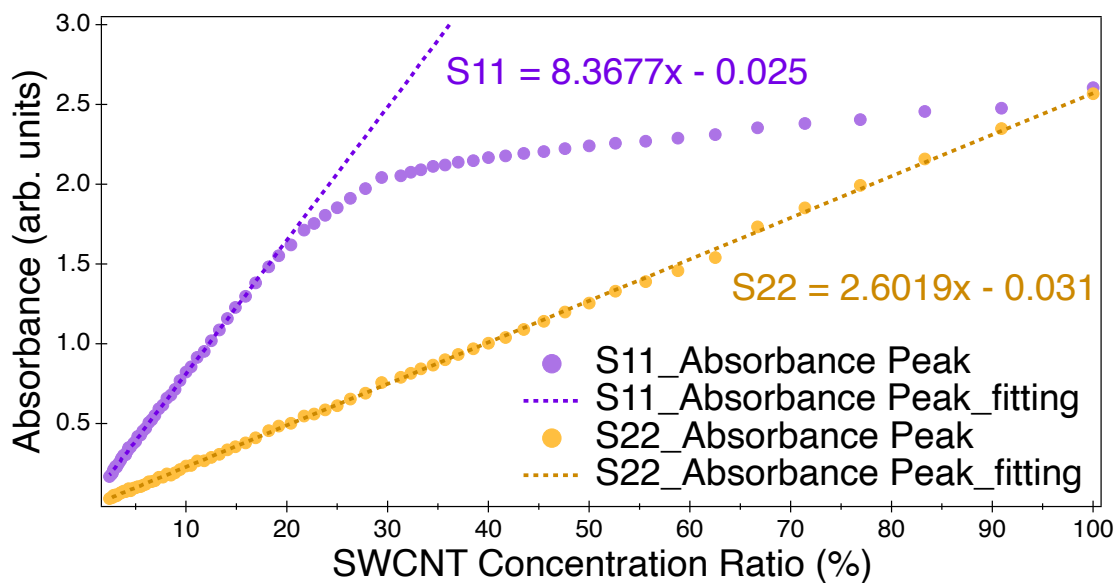


Figure 5.10: Plots of S_{11} and S_{22} peak intensities as a function of relative [SWCNT](#) concentration. The S_{11} peak exhibits a linear relationship within the low concentration regime, with a best-fit line applied to data below 17% relative concentration.

centration range. Linear regression analysis of the low concentration regime for S_{11} and the full range for S_{22} yielded the following equations:

$$\begin{aligned} S_{11} &= 8.3677 \times (\text{relative concentration}) - 0.025 & (R^2 = 0.9996) \\ S_{22} &= 2.6019 \times (\text{relative concentration}) - 0.031 & (R^2 = 0.9996) \end{aligned} \quad (5.1)$$

The deformation of the S_{11} peak at higher concentrations was determined to result from limitations of the UV-vis spectrometer used. Our instrument, the UV-1300PC (VWR®), employs a Si-based detector with a spectral range of 190–1100 nm. However, silicon detectors exhibit a marked drop in sensitivity near the S_{11} region and beyond, towards [NIR](#). This limitation was confirmed by re-measuring the same samples using a LAMBDA 1050+ spectrometer (PerkinElmer), which utilizes a triple-detector system: a photomultiplier tube (PMT) for 200–900 nm, and InGaAs and PbS detectors for the NIR region. With this advanced system, a linear trend for S_{11} was clearly observed even at high [SWCNT](#) concentrations, validating the distortion in our earlier measurements as a detector-related artifact.

The measurements from the LAMBDA 1050+ further confirm the linear dependence

of S_{11} on concentration, with an observed S_{11}/S_{22} peak intensity ratio of approximately 3.22. This high ratio indicates an excellent dispersion quality of the (6,5) SWCNTs. According to established empirical criteria, an S_{11}/S_{22} ratio greater than 3 signifies a highly mono-dispersed and well-sorted sample [10]. Furthermore, the linearity of both S_{11} and S_{22} across a range of concentrations implies that the dispersions are homogeneously prepared and reliably reproducible. Once correlated with absolute SWCNT mass via techniques such as TGA, the absorbance spectra can be used as a predictive tool for estimating the concentration of SWCNTs in unknown solutions.

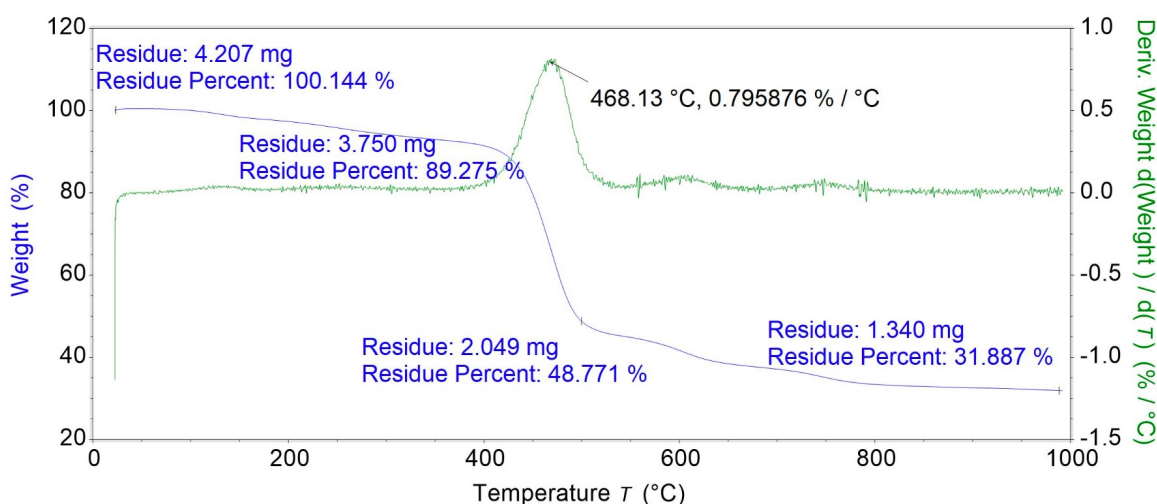


Figure 5.11: TGA analysis of PFO-BPy-dispersed SWCNTs. A total of 4.207 mg of dried dispersion material, containing both SWCNTs and residual PFO-BPy, was collected and analyzed by TGA to determine the relative mass fractions of polymer and nanotube content.

To determine the absolute amount of SWCNTs in the dispersion, a TGA was conducted. 10 mL of PFO-BPy-SWCNT dispersion was dried at 100 °C to remove toluene, yielding a total dried mass of 4.207 mg, which primarily consists of SWCNTs and residual PFO-BPy. The measurement was performed using a TGA Q500 instrument (TA Instruments) with a heating rate of 20 °C min⁻¹ up to 1000 °C under an oxygen atmosphere.

A sharp mass loss was observed at approximately 468 °C, consistent with the thermal decomposition temperature of SWCNTs, which has been reported to occur in the range of 400 °C–500 °C by Mansfield *et al.* [150]. This transition temperature is notably lower than the thermal stability limit of SWCNTs reported to be up to 750 °C

in other studies [204]. The reduced decomposition temperature observed here may be attributed to environmental factors, such as the presence of polymer wrapping or surfactants, which can alter the thermal stability of the nanotubes. Assuming the mass loss at this temperature corresponds exclusively to the decomposition of SWCNTs, the total amount of nanotubes in the sample is estimated to be 1.701 mg per 10 mL of dispersion. The corresponding UV–vis absorbance at the S_{22} peak was measured as 1.3477.

From prior regression using Eq. 5.1, this absorbance corresponds to a relative SWCNT concentration of 52.99%. Therefore, for an ultracentrifuged dispersion exhibiting an S_{22} absorbance of 0.8291 (relative SWCNT concentration 33.06%), the estimated SWCNT content is approximately 1.061 mg in 10 mL. This quantitative estimation provides a valuable reference point for interpreting the PL performance of SWCNT films fabricated from these dispersions.

5.3 Film Fabrication Methods for Single-Walled Carbon Nanotubes

The fabrication of high-quality thin films composed of SWCNTs is a critical step toward the integration of these materials into functional electronic, optoelectronic, and sensing platforms. Over the past two decades, numerous techniques have been developed to deposit, align, and transfer SWCNTs onto various substrates. These methods exhibit significant differences in terms of alignment precision, film uniformity, scalability, material purity, and compatibility with device fabrication processes [97, 173, 112]. Achieving optimal control over these parameters is essential for maximizing device performance and reproducibility.

One of the most widely adopted techniques for fabricating thin films of SWCNTs is **vacuum filtration**, wherein a well-dispersed SWCNT solution is passed through a porous membrane under reduced pressure [224]. During this process, nanotubes are retained on the membrane surface, forming a uniform, mat-like film. This film can be subsequently rinsed to remove surfactants or residual polymers and then transferred onto a target substrate via mechanical pressing or solvent-assisted methods. Vacuum filtration offers relatively good control over film thickness, density, and nanotube alignment [87], while maintaining high material purity. However, the technique is limited in scalability due to the membrane dimensions and involves a delicate transfer step, which may lead to mechanical damage such as wrinkling, folding, or tearing.

Another widely employed technique for fabricating thin **SWCNT** films is **spin coating**, which involves depositing a droplet of nanotube dispersion onto a rapidly rotating substrate. The centrifugal force spreads the solution across the surface, forming a thin, uniform film upon solvent evaporation [81]. Spin coating is advantageous for its simplicity, rapid processing, reproducibility, and compatibility with standard microfabrication workflows. However, this method typically produces films with limited nanotube alignment and offers a relatively narrow range of thickness control, particularly when working with dilute dispersions.

Drop casting and its scalable variant, **blade coating**, are straightforward solution-based techniques for depositing **SWCNT** films [224, 28, 112]. In drop casting, a small volume of nanotube dispersion is pipetted directly onto a substrate and allowed to dry under ambient or controlled conditions, whereas blade coating employs a mechanical blade to spread the dispersion across the surface in a more controlled and scalable manner. These methods enable the fabrication of relatively thick films and are amenable to large-area processing, making them attractive for applications in printable electronics and energy-related devices. However, both approaches commonly suffer from poor film uniformity and random nanotube orientation due to uncontrolled solvent evaporation, leading to effects such as the coffee-ring phenomenon [112].

The **Langmuir–Blodgett (LB) technique** facilitates the formation of monolayer or few-layer **SWCNT** films at the air–water interface, which can subsequently be transferred onto a solid substrate [135]. This method offers precise control over film thickness, nanotube density, and in-plane alignment, particularly when using surfactant- or polymer-stabilized **SWCNT** dispersions. Although **LB** assembly enables the creation of highly ordered and semiconducting-pure films, the process is time-intensive, requires specialized instrumentation, and suffers from limited throughput and scalability.

For direct integration into devices, **floating catalyst chemical vapor deposition (FCCVD)** offers a bottom-up approach by synthesizing and depositing **SWCNTs** in situ during gas-phase growth [187]. This method enables the fabrication of aligned films directly on substrates without the need for post-synthesis processing or transfer. **FC-CVD**-grown films can be scaled up using roll-to-roll systems and adapted for flexible substrates. However, the method typically requires high-temperature processing and often results in residual metal catalyst contamination. Additionally, chirality control remains a significant challenge.

Dip coating involves immersing a substrate into a **SWCNT** dispersion and withdrawing it at a controlled rate, allowing for the deposition of a uniform film due to capillary and gravitational forces [156]. This method is advantageous for coating non-

planar or 3D substrates and enables multi-layer stacking by repeated dipping. Film alignment is generally poor but recently aligned SWCNT films are reported [123]. However, drying dynamics may cause thickness variations.

Emerging large-area deposition techniques include **inkjet printing** and **spray coating**, where SWCNT inks are patterned or atomized onto substrates [136, 108]. These methods are highly compatible with flexible substrates and additive manufacturing, making them attractive for printed electronics. Inkjet printing enables precise patterning, whereas spray coating is better suited for uniform coverage of large surfaces. Nevertheless, both methods are susceptible to issues such as nozzle clogging, ink instability, and limited alignment of the nanotubes.

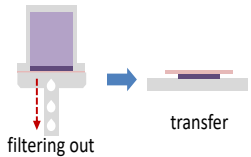
Finally, **dielectrophoresis (DEP)** is a technique that utilizes an alternating electric field to position and align SWCNTs between microfabricated electrodes [176]. This method is particularly effective for high-precision placement of individual nanotubes or small bundles, making it suitable for single-nanotube device fabrication. Although DEP enables excellent alignment and chirality-selective deposition, it is not scalable and is limited to specific geometries.

5.4 Three Film Fabrication Methods for Photoluminescence Examination

Among the various SWCNT film fabrication techniques, vacuum filtration, drop casting, and spin coating were employed to deposit SWCNT layers onto cavity mirrors or buffer layers. These methods were chosen due to their accessibility, simplicity, and suitability for forming uniform SWCNT emission layers with controllable film thickness.

The first method employed for SWCNT film fabrication was vacuum filtration. In this technique, a dispersion of SWCNTs, stabilized by either a surfactant (for ATPE sorted) or PFO-BPy, is passed through a porous membrane filter. During the filtration process, the SWCNTs are retained on the membrane surface, forming a uniform film, while the majority of the dispersing agents are removed with the filtrate. Although small amounts of surfactant or PFO-BPy may remain within the film, their concentrations are substantially reduced relative to the starting dispersion. This efficient reduction in dispersant content is believed to enhance the packing density of SWCNTs within the film, thereby improving PL performance. Owing to its simplicity, effectiveness, and

Table 5.1: Summary of three SWCNT film fabrication methods used for PL examination.

	Vacuum filtration	Drop casting	Spin coating
Setup			
Pros	Dense SWCNT film Filtering out Flexible film position	Easy process Thick film	Easy process Spread out Multi-layer
Cons	Membrane restriction	Uniformity Roughness	Uniformity
For PL	SWCNT density variation	Thick SWCNT layer	Multi-SWCNT layer

ability to produce high-density, high-quality films, vacuum filtration was selected as a preferred fabrication method for the initial PL examinations.

It is important to note that the membrane types used in vacuum filtration differ depending on the dispersion medium. For surfactant-stabilized SWCNT dispersions, polycarbonate (PC) membranes are used, which are later dissolved using N-Methyl-2-Pyrrolidone (NMP). However, since PC membranes are incompatible with toluene, the solvent used in PFO-BPy dispersions, mixed cellulose ester (MCE) membranes are employed instead, which can be dissolved using acetone. The specific conditions are summarized as follows:

- **Surfactant dispersion:** PC membrane, dissolved using NMP
- **PFO-BPy dispersion:** MCE membrane, dissolved using acetone

The volume of dispersion applied during filtration is adjusted based on the desired final amount of SWCNTs in the film. Once vacuum filtration is complete, the resulting membrane-bound SWCNT films are transferred to target substrates through the following procedure:

► **Vacuum filtration membrane transfer recipe:**

1. Preparation of the filtered membrane

The membrane containing the SWCNT film is trimmed to an appropriate size for transfer.

2. Adhesion promotion

A single drop of water (for surfactant films) or (isopropyl alcohol (IPA), for PFO-BPy films) is applied to the substrate surface to facilitate adhesion.

3. Membrane transfer and pressing

The membrane is placed onto the wetted substrate with the SWCNT side facing down. A Kimwipe is placed over the membrane, and gentle, uniform pressure is applied to promote conformal contact and adhesion of the SWCNT film to the substrate.

4. Residue removal

Any remaining water or IPA trapped between the membrane and substrate is gently removed to prepare the sample for the subsequent membrane dissolution step.

5. Membrane dissolution

The sample is immersed in NMP (for surfactant-based films) or acetone (for PFO-BPy-based films) for one hour to fully dissolve the membrane. Fresh solvent is used to rinse the sample to ensure complete membrane removal.

6. Solvent exchange and final cleaning

The sample is then soaked in fresh IPA for an additional hour and rinsed again with clean IPA to remove residual NMP or acetone and other impurities.

7. Drying

Finally, the substrate is dried on a hot plate at 120 °C for one hour to remove any remaining solvent and enhance the adhesion and uniformity of the SWCNT film.

This transfer procedure ensures high-quality, residue-free SWCNT films suitable for subsequent photoluminescence and device fabrication studies.

The ATPE-sorted SWCNT dispersions are unsuitable for drop casting and spin coating due to their inherently low viscosity. In contrast, the viscosity of PFO-BPy-based dispersions can be tuned by adjusting the polymer concentration, which plays a crucial role in enabling film formation. A higher viscosity promotes better wetting and adhesion of the dispersion onto the substrate, facilitating the formation of uniform films. When the PFO-BPy concentration is at its standard value of 1 mg/mL, the viscosity is insufficient for effective film deposition via drop casting or spin coating. To address this, the PFO-BPy concentration must be increased to at least 5 mg/mL by adding additional polymer.

► **Key considerations for drop casting:**

- **PFO-BPy concentration:** Should be increased to more than 5 mg/mL for adequate viscosity and film formation.
 - * Initial concentration: 1 mg/mL
- **Substrate alignment:** Ensure that the substrate is placed on a perfectly flat and level surface to promote uniform spreading of the droplet.
- **Dispensing volume:** Approximately 5 μ L of dispersion is sufficient for a 1 cm $\times$ 1 cm substrate area.
- **Drying:** Allow the droplet to dry naturally for several minutes in ambient conditions to form a continuous film.

► **Key considerations for spin coating:**

- **Dispensing volume:** Approximately 7.5 μ L of dispersion is recommended per 1 cm $\times$ 1 cm substrate to ensure complete coverage.
- **Dispensing area:** The dispersion should be deposited at the center of the substrate and must adequately spread to cover the entire surface area before spinning.
- **Spin coating parameters:**
 - **Step 1:** 500 rpm for 5 seconds, with a ramp rate of 100 rpm/s (to distribute the solution evenly across the substrate).
 - **Step 2:** 5000 rpm for 60 seconds, with a ramp rate of 500 rpm/s (to form a uniform and thin film).
 - **Step 3:** 0 rpm (to stop the spin process).

5.5 Photoluminescence Spectroscopy and Characterization

5.5.1 Liquid and film

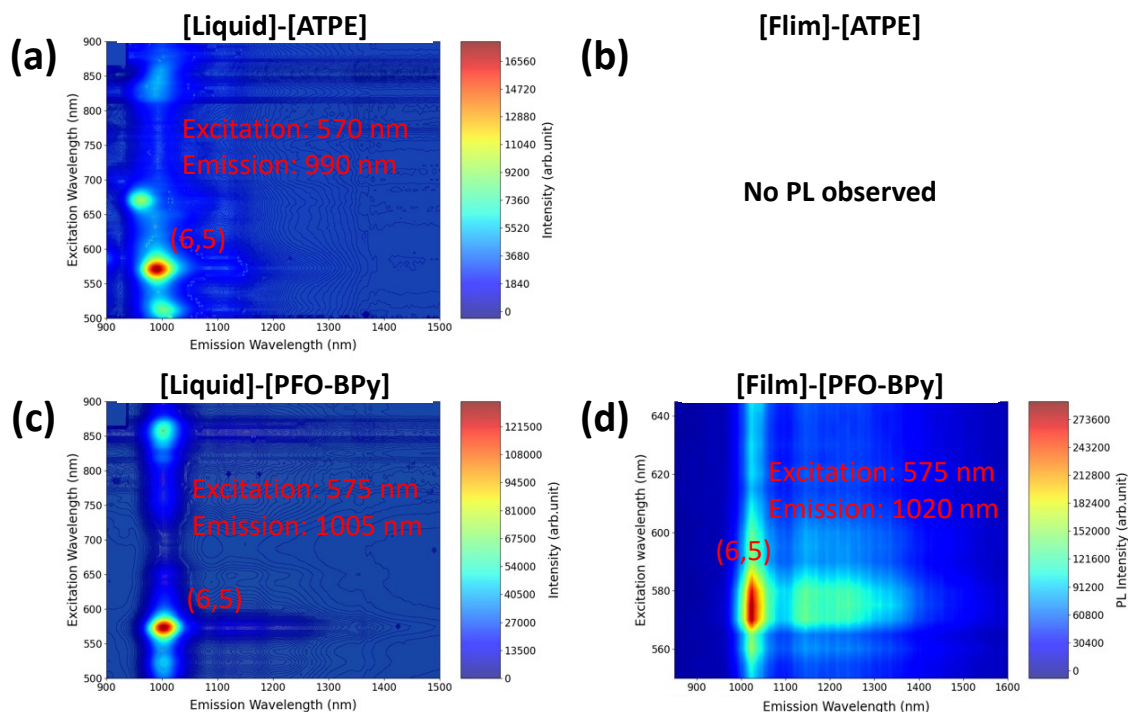


Figure 5.12: 2D PL intensity maps of SWCNT samples: (a) liquid dispersion sorted by ATPE, (b) film fabricated from ATPE-sorted dispersion (no detectable PL signal), (c) liquid dispersion sorted by PFO-BPy, and (d) film fabricated from PFO-BPy-sorted dispersion.

To evaluate the initial PL properties, both solution-based and film-based samples were prepared using two different SWCNT sorting methods: ATPE and PFO-BPy. Each sorting method yielded a (6,5)-dominant dispersion, and two types of samples, liquid and thin film, were fabricated from each, resulting in four distinct samples, as shown in Fig. 5.12.

The left column of the figure presents PL maps for the liquid samples: Fig. 5.12(a) for ATPE and Fig. 5.12(c) for PFO-BPy. While the ATPE-sorted dispersion is primarily (6,5), an additional (8,3) chirality signal is observed. In contrast, the PFO-BPy-sorted

dispersion exhibits a highly purified (6,5) emission, with negligible signals from other chiralities. In both cases, the emission associated with the (6,5) tube's S_{11} transition appears near 1000 nm, with excitation centered around 575 nm. Notably, the PL intensity of the PFO-BPy sample is more than seven times stronger than that of the ATPE sample, indicating a higher purity and better emission efficiency in the former.

These trends extend to the solid-state samples shown in Fig. 5.12(b) and (d). The film fabricated from the ATPE dispersion does not exhibit any detectable PL, which may be attributed to the presence of metallic SWCNTs, as indicated by the absorbance spectrum. Metallic tubes are known to quench exciton emission, an effect that can be exacerbated in films where inter-tube distances are reduced. Conversely, the film prepared from the PFO-BPy dispersion retains clear PL emission, with excitation and emission characteristics consistent with the liquid-phase results, demonstrating the suitability of this method for fabricating high-quality emissive SWCNT films.

5.5.2 Single-Walled Carbon Nanotube Amount in a Film

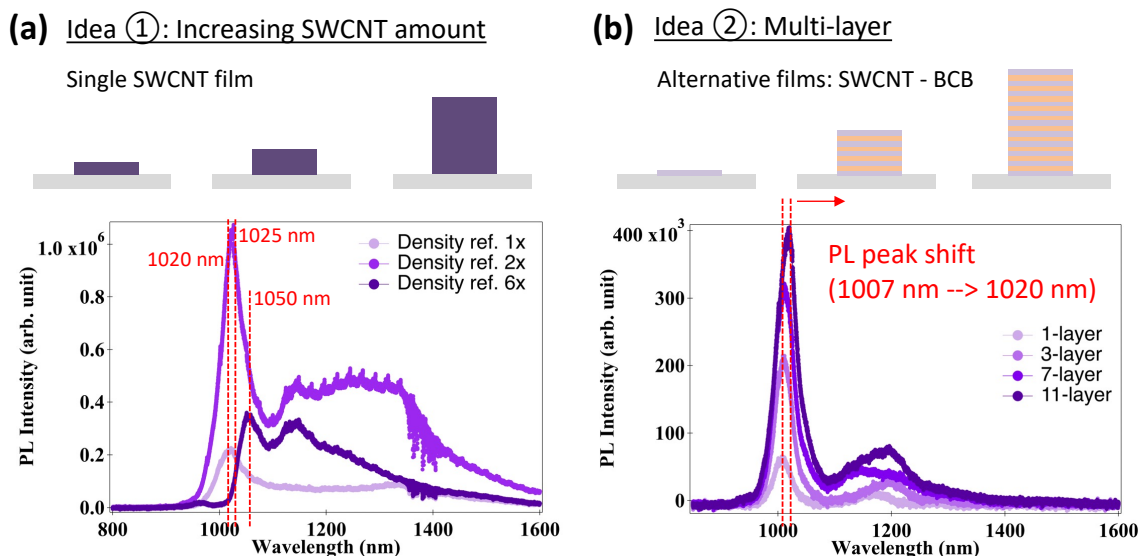


Figure 5.13: PL enhancement attempt of SWCNT films through (a) increasing the amount of SWCNTs in a single film, and (b) stacking multiple SWCNT film layers.

As might be intuitively expected, the simplest way to enhance the PL of SWCNT films is by increasing the amount of SWCNTs within the film. This can be achieved

either by increasing the film thickness in a single layer or by stacking multiple SWCNT film layers. The former approach, thickness enhancement in a single layer, can be readily realized through the vacuum filtration method. As shown in Fig. 5.13(a), we prepared three SWCNT films with different thicknesses and measured their PL properties. The results indicate that, as the film thickness increases, the main PL peak intensity appears to increase when comparing the thinnest and intermediate-thickness films. However, a red shift of the peak wavelength is also observed, along with an increase in intensity across the 1100 nm to 1400 nm spectral range.

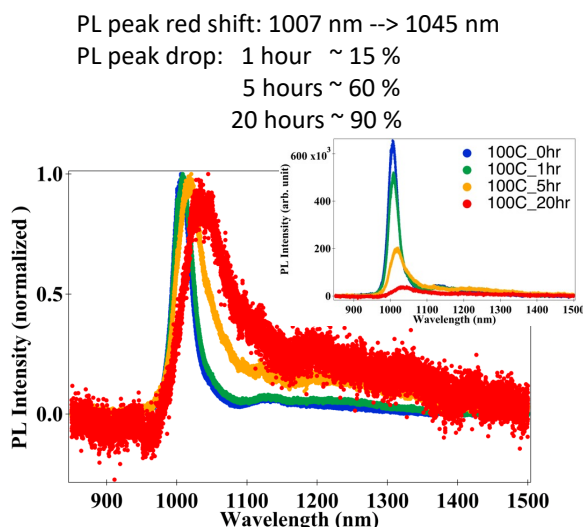
Contrary to expectations, further increasing the film thickness to the thickest level did not lead to higher PL intensity. Instead, the overall PL intensity decreased, the peak wavelength shifted further toward the red, and the spectral shape in the 1100 nm to 1400 nm region became distorted. These observations suggest that beyond a certain thickness, reabsorption, scattering, or aggregation effects may dominate, leading to PL quenching.

The multilayered structure was fabricated using the spin-coating method. To assemble the layers, we deposited SWCNT films sequentially, with a dielectric spacer, BCB, inserted between each film layer. A total of four layers were prepared for comparison, as illustrated in Fig. 5.13(b). As shown in the PL measurement results, the PL intensity increased with the number of stacked layers. However, a consistent red shift of the emission peak was also observed as the number of layers increased. This suggests that, similar to the case of increasing thickness in a single-layer film, optical interactions such as reabsorption or interlayer coupling may contribute to the spectral shift and also the spectral shape in the 1100 nm to 1400 nm region became distorted.

5.5.3 Film Annealing and Repeated Measurements

There are several challenges associated with SWCNT films. One of the common practices to improve film stability is thermal annealing; however, we observed that annealing leads to photoluminescence (PL) degradation. As shown in Fig. 5.14(a), the main PL peak intensity decreased by up to 90% after 20 hours of annealing at 100 °C. Additionally, a noticeable red shift of the peak wavelength was observed. Although the extent of degradation varied, similar trends were confirmed at other temperatures such as 80 °C and 120 °C. Furthermore, as shown in Fig. 5.14(b), repeated PL measurements also led to a gradual decrease in peak intensity. While no significant red shift was observed in this case, the spectral shape in the range of 1100 nm to 1400 nm showed noticeable distortion. These observations indicate that both thermal treatment

(a) Issue ①: Annealing



(b) Issue ②: Number of measurements

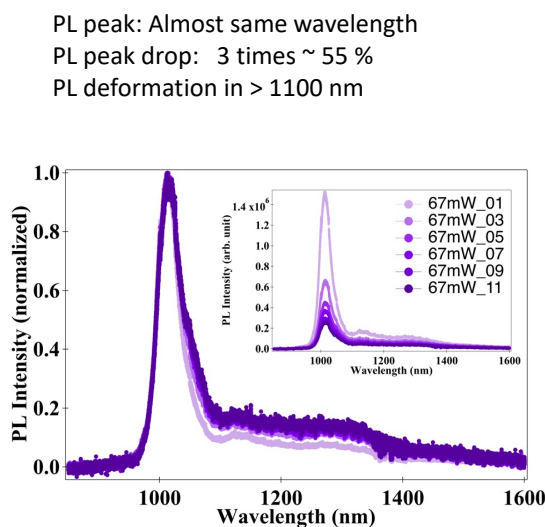


Figure 5.14: PL degradation of SWCNT films observed due to (a) thermal annealing and (b) repeated photoluminescence measurements.

and prolonged optical excitation can degrade the PL properties of SWCNT films.

In both cases, a decrease in PL intensity, a red shift of the emission peak, and distortion of the spectral shape in the 1100 nm to 1400 nm range were observed. These phenomena are commonly attributed to thermally induced changes in the PFO-BPy wrapping, which likely lead to a reduced inter-tube distance between SWCNTs. This closer proximity facilitates exciton quenching, resulting in the observed degradation of the PL signal.

5.5.4 Lessons from Photoluminescence Measurements

Based on these observations, a *guiding principle* for SWCNT film fabrication was established to maximize PL performance: minimize the overlap between individual SWCNTs. Reducing overlap helps to suppress reabsorption of emitted PL within the film, thereby enhancing the external emission efficiency.

Another important consideration is to maintain sufficient spacing between SWCNTs. Although no detailed theoretical model has been developed in this study, it is important to note that most available energy diagrams are based on isolated, individual SWCNTs.

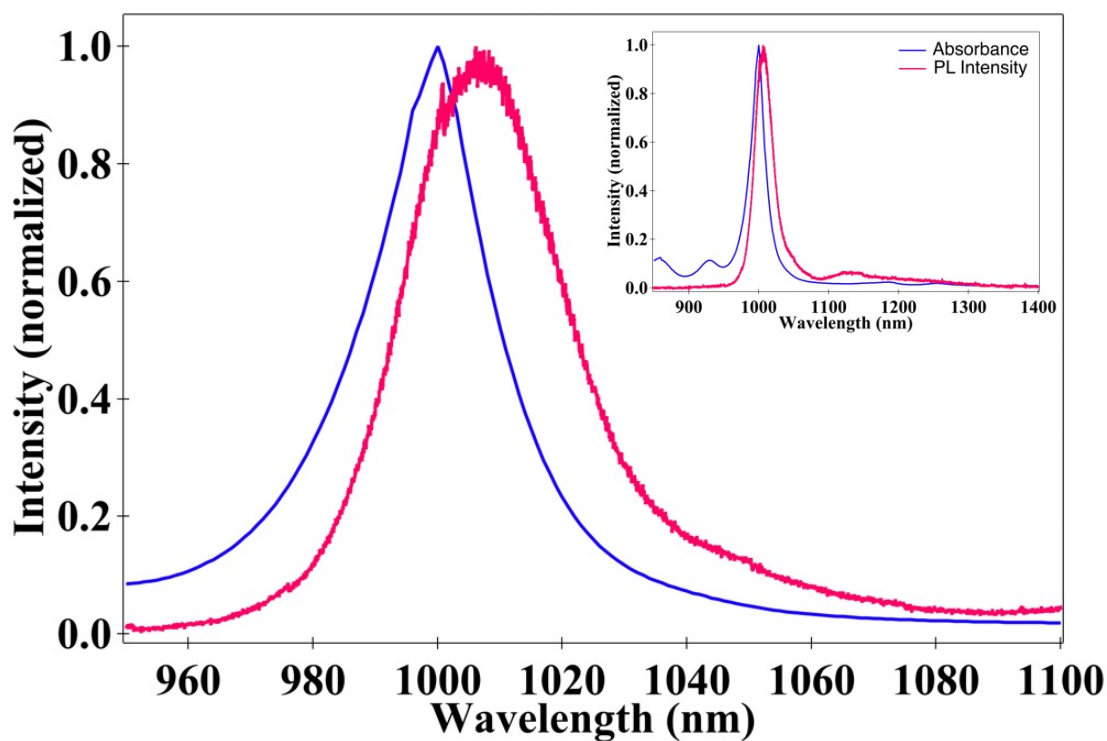


Figure 5.15: Both the absorbance and PL spectra are plotted simultaneously for direct comparison.

It is presumed that aggregated SWCNTs exhibit altered electronic structures, such as a reduced bandgap or distorted energy levels, which can significantly degrade PL quality. Therefore, ensuring well-dispersed and spatially separated SWCNTs is essential for preserving the intrinsic optical properties of the material.

Chapter 6

Design, Fabrication, and Characterization of Microcavities

The reflection studies presented in Chapter 2 indicate that a target reflectivity exceeding 99.97% is required, which is expected to be achieved using a DBR structure. Nonetheless, as discussed in Chapter 4, Au mirrors have been in recent studies on SWCNT exciton-polaritons in SWCNTs, primarily due to their ease of fabrication and broadband reflectivity. To address diverse experimental requirements, such as spectral range, device architecture, and fabrication compatibility, and to facilitate a direct comparison between different optical configurations, both Au and DBR mirrors are utilized in the fabrication of our devices in this work.

6.1 Comparative Analysis of Materials for Cavity Mirrors

Ag, Au, and Al are widely used as metallic mirrors for applications spanning the visible to near-infrared (NIR) spectral regions. Their reference reflectance spectra are presented in Fig. 6.1(a) [40]. While all three metals exhibit reflectance values exceeding 95% across much of the spectrum, their performance in the visible range differs significantly. The reflectance of Ag rises sharply between 400 nm and 500 nm, whereas that of Au increases markedly between 500 nm and 600 nm. In contrast, Al maintains a relatively consistent reflectance above 90% across the entire visible range.

Among these candidates, Au was selected for this study based on the excitation and emission characteristics of (6,5) SWCNTs. As shown in the 2D PL map in Fig. 5.12(a),

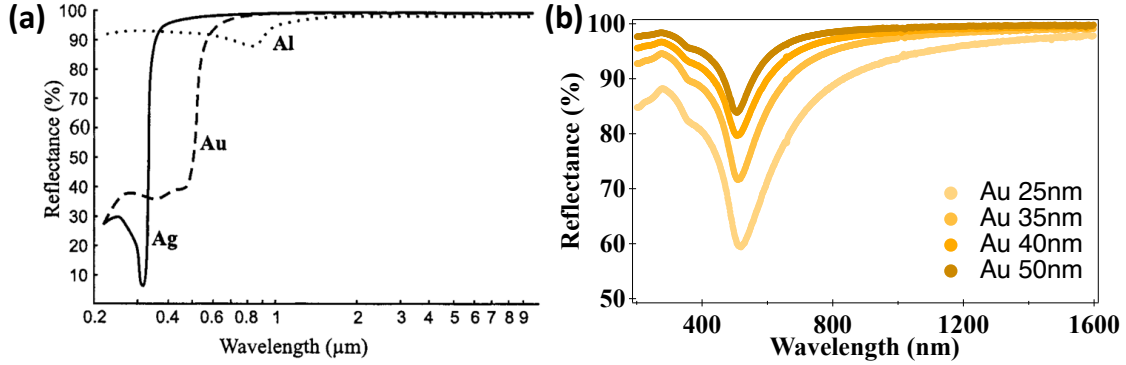


Figure 6.1: (a) Reference reflectance spectra of representative metal mirrors: Ag, Au, and Al, adapted from [40]. (b) Reflectance spectra of Au as a function of film thickness, illustrating the influence of thickness on optical performance.

the optimal excitation wavelength corresponds to the S_{22} transition near 575 nm in the visible region, while emission occurs above 1000 nm the optimal excitation wavelength corresponds to the S_{22} transition near 575 nm in the visible region, while emission arises from the S_{11} transition, occurring at wavelengths above 1000 nm in the NIR. This spectral profile aligns well with the reflectance characteristics of Au, making it a suitable choice for maximizing PL efficiency in transmission-based optical measurements.

The reflectance of Au films also depends strongly on thickness. To investigate this behavior, four Au films of varying thickness (25, 35, 40, 50 nm) were deposited on fused silica substrates using metal evaporation. Their corresponding reflectance spectra are plotted in Fig. 6.1(b). These measurements were performed using an M-2000DI ellipsometer (J.A. Woollam Co.) and verified via transmission measurements. Assuming negligible scattering and absorption, reflectance was estimated by subtracting the transmittance from 100%. The absolute reflectance values at key wavelengths are summarized in Table 6.1. Three wavelengths were considered: 575 nm (the excitation peak), 1010 nm (the PL emission maximum), and a secondary reference wavelength above 1010 nm.

In practical device fabrication, Au film thickness typically ranges from 25 nm to 60 nm. Given the transmission-based measurement setup used in this study, minimizing reflectance at the excitation wavelength (575 nm) is essential to ensure sufficient pump light reaches the active layer. Therefore, the maximum allowable Au thickness was set to 50 nm, which provides a reflectance of approximately 99.48% at the PL peak wavelength (1010 nm), a suitable trade-off between excitation transmission and PL col-

Table 6.1: Reflectance of Au with varying thickness at different wavelengths.

Au thickness	Reflectance (%)		
	575 nm	1010 nm	1200 nm
25 nm	67.41	95.12	96.03
35 nm	81.16	98.09	98.42
40 nm	87.63	98.87	99.05
50 nm	91.97	99.48	99.55

lection efficiency.

Table 6.2: Refractive index (n) and extinction coefficient (k) for different materials at S_{11} transitions of (6,5), (7,5), and (7,6) chiralities. The data are extracted from <https://refractiveindex.info/>.

Material	Ref.	(6,5) S_{11}		(7,5) S_{11}		(7,6) S_{11}		Result
		977 nm n	k	1024 nm n	k	1120 nm n	k	
α -Si	Pierce et al. 1972	3.656	-0.004	3.616	-0.001	3.572	0.000	Highest n For substrate Low n / low k
Si	Schineke et al. 2015	3.581	0.00075	3.567	0.000284	3.540	1.71E-05	
SiO ₂	Lemarchand 2013	1.468	1.797E-79	1.467	-4.998E-85	1.467	5.198E-112	
Si ₃ N ₄	Luke et al. 2015	2.015	0.000E+00	2.013	0.000E+00	2.009	0.000E+00	Lowest n / High k No k data No k data
ZnO	Aguilar et al. 2019	1.747	0.023	1.745	0.022	1.742	0.021	
Al ₂ O ₃	Querry 1985	1.229	8.131	1.126	8.659	1.070	9.722	
MgO	Stephens et al. 1952	1.723		1.722		1.721		
HfO ₂	Al-Kuhaili 2004	1.882		1.882		1.880		
TiO ₂	Starkar et al. 2019	2.077	0.000E+00	2.074	0.000E+00	2.069	0.000E+00	
Nb ₂ O ₅	Lemarchand 2013	2.260	-7.105E-49	2.256	1.976E-54	2.250	-2.108E-81	

For dielectric mirrors, the refractive index (n) and the extinction coefficient (k) are critical parameters. The refractive index n directly influences the reflectance of the mirror, as described in Eq. 2.10, while the extinction coefficient k is associated with material absorption, where a value close to zero or lower is preferred to minimize optical losses. Table 6.2 compiles the refractive index (n) and extinction coefficient (k) of various materials at three relevant wavelengths: 977, 1024, and 1120 nm. According to the reflectivity equation, a larger contrast in refractive indices between the two materials forming the multilayer stack results in higher reflectivity, reducing the number of layers required to achieve a given reflectance. Among commonly used dielectric materials in Table 6.2, amorphous silicon (α -Si) exhibits the highest refractive index, while Al₂O₃ shows one of the lowest. Note that the selection of dielectric materials must take into account several factors, including compatibility with available fabrication techniques,

particularly when alternating layer stacks are constructed within a single deposition system, to optimize process efficiency and maintain fabrication consistency.

Dielectric mirrors to form optical cavities with high reflectivity and low absorption are typically fabricated using thin-film deposition techniques such as molecular beam epitaxy, physical vapor deposition (such as sputtering and evaporation), and [plasma enhanced chemical vapour deposition \(PECVD\)](#). Among these, [PECVD](#) is a commonly used technique due to its relatively fast deposition rate and compatibility with a range of substrates; however, it generally yields films with lower density compared to sputtering. Considering the equipment available at the Quantum-Nano Fabrication and Characterization Facility (QNFCF) and the material compatibility under policy, the following combinations are deemed feasible:

Available dielectric mirror combinations:

- **PECVD:** SiO_2 : α -Si
 - * Offers a large refractive index contrast
 - * Non-zero extinction coefficient (k) below 950 nm
- **PECVD:** SiO_2 : SiN_x
 - * Zero extinction coefficient (k)
 - * Good transparency in the target spectral region
- **Sputter:** SiO_2 : TiO_2
 - * A well-established and commonly used combination for [DBR](#) structures

Before transitioning to the full planar microcavity structure, it is essential to evaluate and compare metal-based mirrors and dielectric [DBR](#) in terms of their spectral performance and reflectance characteristics. Multilayer [DBR](#) is formed by alternating high- and low-index materials. The choice of mirror material must consider not only the peak reflectance but also the spectral bandwidth over which high reflectivity is maintained. As illustrated in Fig. [6.1](#), metallic mirrors typically exhibit a broad and relatively flat spectral reflectance response, especially in the [NIR](#) range. This makes them suitable for broadband applications where consistent reflectivity over a wide spectral range is required. However, despite their simplicity in fabrication and broadband response, metals generally offer limited peak reflectance compared to [DBRs](#). Figure [6.2](#) directly compares the reflectance spectra of Au and [DBR](#) mirrors.

In contrast, [DBRs](#) exhibit a characteristic high-reflectivity spectral region known as the stopband. This stopband arises from constructive interference of reflected waves at

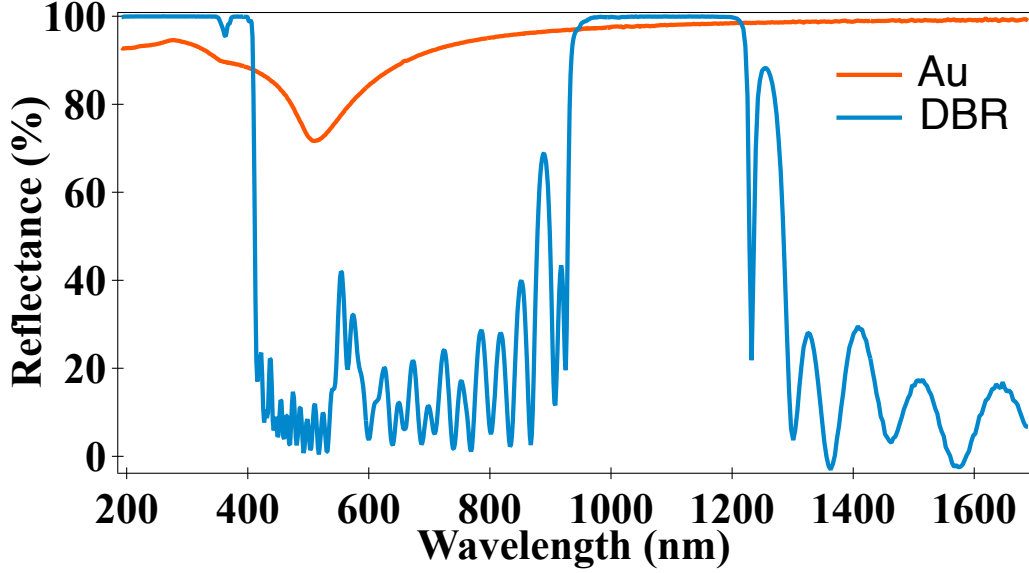


Figure 6.2: Representative reflectance spectra of Au and a DBR.

the interfaces between alternating high- and low-refractive-index layers. The spectral width of the stopband depends on the refractive index contrast and is given by:

$$\text{Stopband} = \frac{\lambda_{\text{mid}}}{\pi} \arcsin\left(\frac{n_2 - n_1}{n_2 + n_1}\right), \quad (6.1)$$

where n_1 and n_2 are the refractive indices of the low- and high-index materials, respectively, and λ_{mid} is the central wavelength of the stopband, estimated as $\lambda_{\text{mid}} = 2dn_{\text{eff}}$, with d being the physical thickness of each layer and n_{eff} the effective refractive index, typically the average of n_1 and n_2 .

The refractive index contrast between the DBR layers is therefore a key design parameter, as it directly impacts both the stopband width and the maximum achievable reflectance. However, since each DBRs exhibit a finite reflectivity bandwidth, careful consideration must be given to whether the desired application requires a broadband mirror (favoring metals) or a narrowband, high-reflectivity mirror (favoring DBRs). By leveraging the inherent optical properties of the constituent materials and ensuring their fabrication compatibility, DBR structures can be precisely designed to achieve high reflectance in the desired spectral range, whose details are discussed in the next

section.

6.2 Fabry-Pérot Cavity Design for Single-Walled Carbon Nanotube Films

According to our comprehensive review of resonator architectures, the [FP](#) cavity has been selected as the foundational platform for developing novel optical devices including a new type of lasers. This choice relies on the simplicity, scalability, and well-established capability to support strong optical feedback, which are critical features for prototyping and advancing integrated photonic devices.

[SWCNTs](#) have been chosen as the active gain medium due to their unique and exceptional optical characteristics, particularly for [NIR](#) semiconductor laser applications. Unlike traditional semiconductor materials, [SWCNTs](#) offer broadband and chirality-dependent tunable emission across the NIR region, a spectral range that remains a challenge to access with many conventional III-V or II-VI semiconductors. Note that their strong excitonic transitions for room-temperature stability and ultra-thin form factor further position them as ideal candidates for integration into compact photonic systems. A significant advantage of [SWCNTs](#) lies in their material adaptability. Once a reliable fabrication and processing recipe is established, the emission wavelength can be tuned without modifying the overall fabrication methodology, simply by selecting [SWCNTs](#) with the desired chirality. This flexibility stands in stark contrast to conventional semiconductors, where material specific processes and material composition are typically required for different wavelength ranges. Furthermore, the solution-processable nanomaterials facilitate scalable, high-volume manufacturing. Given these strengths, [SWCNTs](#) represent a promising path forward in the pursuit of compact, tunable NIR lasers. This section details the design of the planar FP cavities tailored for near-infrared emissions (~ 1000 nm) from (6,5)-[SWCNT](#) films and reports on the fabrication outcomes of the implemented structures.

Transfer Matrix Calculations

For dielectric mirror design, the transfer matrix method is used to simulate the reflection, transmission, and absorption coefficients, as it is the standard analytical approach for modeling the optical behavior of multilayer thin-film structures [\[117\]](#). In

order to optimize the DBR mirrors with $Q > 1000$ for fabrication, key material parameters, the refractive indices of the alternating low- and high-index layers (n_1, n_2) as well as the number of layer pairs (N), are systematically varied for given the target cavity wavelength, which is at the center of the S_{11} exciton transition wavelength from the (6,5)-SWCNT film, ensuring maximal reflectivity and spectral alignment with the emission peak.

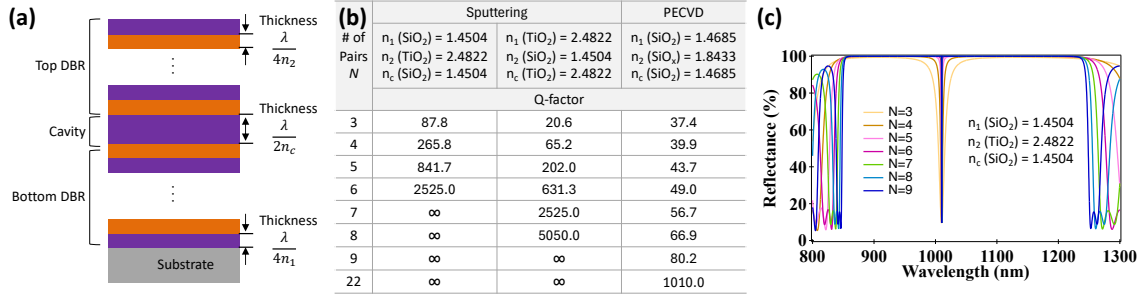


Figure 6.3: Transfer matrix simulation results. (a) Schematic of the microcavity structure without an embedded gain medium. (b) Comparison of three different sample configurations, showing the variation in Q-factor as a function of the number of DBR pairs. (c) Representative reflectance spectra for a $\text{SiO}_2/\text{TiO}_2$ multilayer structure.

To target the main PL peak of the (6, 5) chirality at 1010 nm (λ), a planar microcavity was designed accordingly. As shown in Fig. 6.3(a), the microcavity structure follows the previously described configuration, with the only difference being the absence of the gain medium, resulting in an empty cavity. The cavity material (n_c) is identical to that of the first layer DBR material (n_1), while the thickness was tailored to form a standing wave at the target wavelength (λ), specifically designed as $\lambda/(2n_c)$.

The subsequent section will discuss material combinations that are compatible with experimental fabrication. Among those, we examine and simulate two DBR material combinations: SiO_2 and TiO_2 (compatible with sputtering), and SiO_2 and SiNx (compatible with PECVD). In particular, for the $\text{SiO}_2/\text{TiO}_2$ pair, we compared two stacking orders, one where SiO_2 is deposited first (material $n_1 = \text{SiO}_2$), and the other where TiO_2 is deposited first. The resulting Q-factors were simulated for planar microcavities with varying numbers of DBR pairs, and the outcomes are summarized in Fig. 6.3(b).

As expected, due to the higher refractive index contrast (i.e., $|n_1 - n_2|$), the $\text{SiO}_2/\text{TiO}_2$ combination exhibits significantly higher Q-factors with fewer DBR pairs compared to the SiO_2/SiNx combination. In the case of the $\text{SiO}_2/\text{TiO}_2$ combination, a Q-factor exceeding 1000 can be achieved with as few as 6 to 7 DBR pairs. In contrast, the SiO_2/SiNx

combination requires at least 22 pairs to reach a comparable **Q-factor**. (* Note: For the $\text{SiO}_2/\text{TiO}_2$ combination, the simulation was performed with a wavelength resolution of 0.1 nm, which can result in unrealistically high **Q-factors** under certain conditions.) A particularly noteworthy finding is that microcavities with SiO_2 as the first **DBR** layer achieve higher **Q-factors** with fewer pairs than those where TiO_2 is deposited first. This behavior can be attributed to the refractive index contrast at the air–**DBR** interface. Assuming the refractive index of air is 1, the reflection at the first interface depends on the contrast between air and the topmost **DBR** layer. If the first layer is a low-index material, the index contrast is smaller, leading to reduced reflection at the surface. This allows more light to enter the **DBR** structure, thereby enhancing the internal reflection and resulting in an overall higher reflectivity. The simulated reflectance spectrum of the $\text{SiO}_2/\text{TiO}_2$ structure, with SiO_2 as the first grown layer, is shown in Fig. 6.3(c).

It is worth to note that the calculation assume lossless materials; therefore, the results are idealized reflectance values. While deviations are expected in practical implementations due to material absorption and imperfections, these simulation results serve as a valuable reference for guiding prior to fabrication.

6.3 Fabrication of Mirrors and Planar Microcavities

Table 6.3: Comparison of different mirror materials and deposition methods.

	Metal	Dielectric			
Material	Au	$\text{SiO}_2/\text{a-Si}$	$\text{SiO}_2/\text{SiN}_x$	$\text{SiO}_2/\text{TiO}_2$	$\text{SiO}_2/\text{TiO}_2$
n	–	1.46 / 3.38	1.46 / 1.87	1.46 / 2.06	–
Equipment	E-beam / DC sputtering (QNFCF)	PECVD (QNFCF)	PEDVD (QNFCF)	RF sputtering (QNFCF)	Ion E-beam (Helia)
Layers	1	9 pairs	30 pairs	15 pairs	16 pairs
Stopband	–	~300 nm	~120 nm	~200 nm	~200 nm
Pros	Easy	Short growth time Wide stopband	Short growth time	–	High quality
Cons	Low reflectance	Heat High absorption	Heat Narrow stopband Too many layers	Long growth time	Long lead time

The preceding sections have detailed the design of mirrors and planar microcavities, with particular emphasis on material selection and associated fabrication techniques. Considering these aspects, five distinct mirror types were developed: one

metal-based and four using different dielectric layer combinations. The resulting FP-cavity structures without gain media are systematically summarized in Table 6.3. The table presents a comparative overview of the fabricated mirror types and cavity structures, highlighting key parameters such as material composition, thickness, fabrication methods, and resulting optical performance metrics.

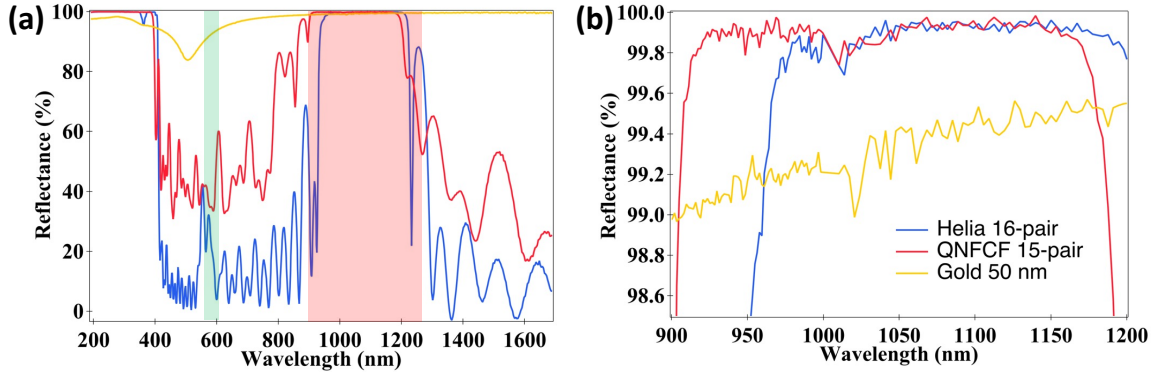


Figure 6.4: Reflectance comparison among Au (50 nm), sputtered DBR, and ion beam-evaporated DBR: (a) over the full wavelength range, and (b) in the red-shaded stopband region.

Mirror Examination

The first mirror fabrication study focused on a Au layer, whose reflectance behavior as a function of thickness is shown in Fig. 6.1(b). The Au mirrors were deposited using an electron-beam (e-beam) evaporator (Angstrom Engineering®), which offers a significantly faster deposition rate, approximately 40 times faster than conventional dielectric film deposition via RF sputtering. Although Au can also be deposited using a DC sputtering system, e-beam evaporation remains roughly 2.6 times faster. While sputtering is known to yield films with higher density, the optical performance (i.e., reflectance) of the Au films fabricated by e-beam evaporation was found to be sufficient for our purposes. Due to its ease of use and high throughput, the Au mirror was employed as a baseline for comparison in data acquisition.

Dielectric mirrors were fabricated using PECVD, RF sputtering and ion-assisted e-beam evaporation methods. PECVD was particularly attractive due to its fast growth rate, comparable to that of e-beam evaporation, and the availability of several compatible materials. Among options, notably, amorphous silicon (α -Si) was considered for

use in DBR fabrication due to its high refractive index ($n > 3$), which enables a broad stopband width of approximately 300 nm. However, α -Si exhibits significant optical absorption below 950 nm, limiting its suitability for certain applications. Another attempt using a combination of SiO₂ and SiNx was made to mitigate this issue. However, due to the relatively small refractive index contrast between these materials ($|n_1 - n_2| = 0.41$) a higher number of layer pairs ($N = 30$) was required to achieve high reflectivity as observed in the simulation section. This increased stack thickness introduced mechanical stress and resulted in cracking, primarily caused by the elevated process temperatures, 250 °C for α -Si/SiO₂ and 330 °C for SiNx/SiO₂. Additionally, PL studies on SWCNT films revealed a degradation in PL intensity following thermal exposure, indicating that PECVD is not suitable for fabricating optical structures intended for such sensitive devices.

Consequently, attention shifted to the conventional high-index contrast dielectric pair TiO₂/SiO₂, fabricated using RF sputtering. From reflectance simulations and index pair studies, it was determined that more than 15 layer pairs are needed to achieve reflectance exceeding 99.97%, corresponding to an estimated Q-factor above 1000. A parallel fabrication was also conducted via commercial coating by Helia Photonics Ltd., using the same material pair but utilizing ion-beam-assisted e-beam evaporation to improve film density and interface quality. Both fabrication approaches yielded comparable stopband widths (~200 nm) and achieved high reflectance (> 99.97%) with 15 and 16 layer pairs, respectively.

Figure 6.4 presents a comparative analysis of reflectance spectra among the Au mirror and the two DBR structures. The full spectral range is shown in Fig. 6.4(a), while a zoomed-in view of the stopband region, from 900 nm to 1250 nm, is provided in Fig. 6.4(b). Around the excitation wavelength of 575 nm (highlighted in green), the ion-beam-assisted DBR shows slightly lower reflectance than the others, potentially improving absorption of the excitation laser. This performance enhancement is attributed to denser and cleaner film interfaces achieved via ion-beam assistance. As anticipated, the reflectance of the Au mirror is lower than that of the DBRs in the stopband region. Nonetheless, both DBR designs exhibit reflectance sufficient for use in planar microcavity structures.

Microcavity with Gain Media

Following mirror studies, planar microcavities with gain media were fabricated and evaluated, as summarized in Table 6.4. Various combinations of mirrors, cavity ma-

materials, and SWCNT films as a gain medium were explored. The allowed cavity modes inside the stopband are primarily governed by the cavity layer and the refractive indices of the constituent materials, both of which can be controlled during design and fabrication. At first, Al_2O_3 and PMMA were initially tested as cavity materials; however, both exhibited undesired absorption within the target wavelength range. In contrast, BCB demonstrated excellent transmission characteristics above 500 nm, making it a suitable candidate for the cavity layer in planar microcavity structures. Additionally, BCB has a refractive index of approximately 1.48 at 1010 nm, which is well-matched with the index contrast required for efficient DBR mirror operation (see Fig. 6.5).

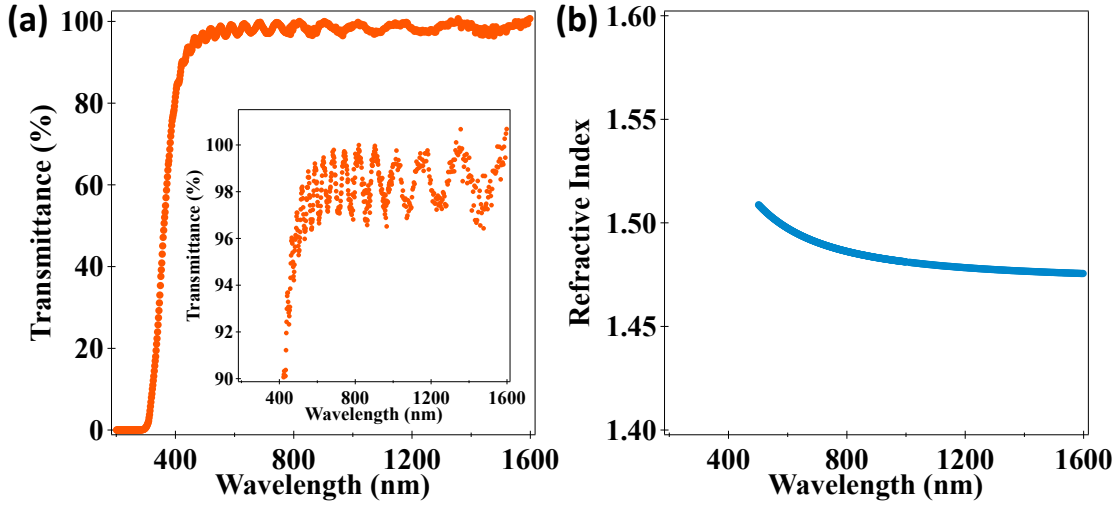


Figure 6.5: Material properties of benzocyclobutene (BCB) film, (a) transmittance and (b) refractive index.

Since the cavity thickness is a key determinant of the resonant wavelength, a reliable and reproducible method for controlling the film thickness was developed. BCB was deposited via spin-coating, with its thickness tuned by adjusting the solution viscosity with solvent T1100. The liquid precursor was the Cyclotene 3000 series (3022-46, Dow Chemical), which yields a film thickness of approximately $2.35\ \mu\text{m}$ when spin-coated at 5000 rpm. To produce thinner films, a dilution protocol was applied, for example, 5.2 mL of T1100 solvent was mixed with 1 mL of 3022-46, and the resulting solution was spin-coated at 5000 rpm. This produced a film with a pre-annealing thickness of approximately 136 nm on a DBR substrate. When a thermally cured film is required, the sample can be baked at 290°C for 3 minutes. This process typically reduces the film thickness by 10%–15%, attributed to polymer densification during crosslinking. The

results of the BCB thickness study are presented in Fig. 6.6. Reference data points extracted from the *Processing Procedures for CYCLOTENE 3000 Series* were plotted alongside experimental results (Fig. 6.6(a)). The data exhibit an exponential dependence of thickness on dilution, well approximated by the relation $y = 0.0604e^{0.0799x}$. A magnified view of the experimental data in the red box is shown in Fig. 6.6(b). Notably, we observed that BCB films deposited on Au substrates were consistently 10%–15% thicker than those deposited on DBR substrates under identical processing conditions. These data are critical for precisely tuning the cavity thickness to target specific resonant wavelengths.

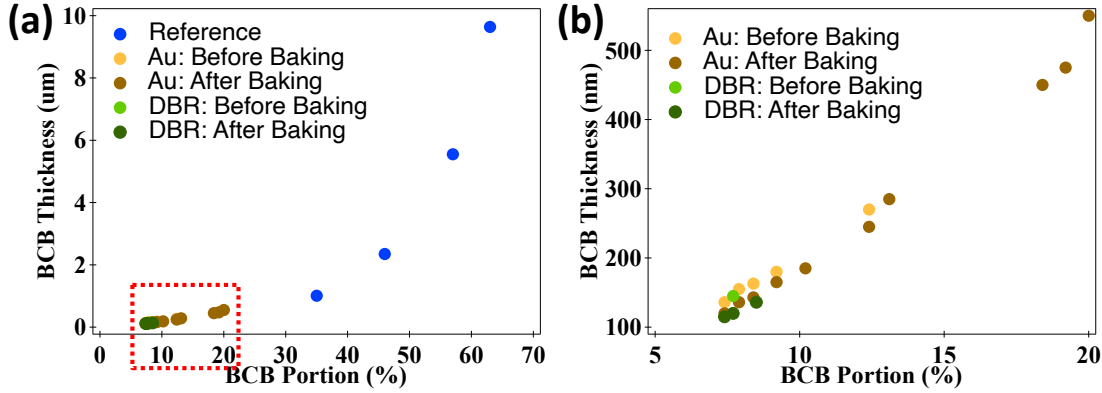


Figure 6.6: BCB spin coating thickness test. Spin coating was performed at 5000 rpm with varying BCB concentrations in the solution. (a) Thickness data for all tested concentrations, including reference points from the *Processing Procedures for CYCLOTENE 3000 Series*. (b) Enlarged view highlighting the measured data points corresponding to low BCB concentrations, indicated by the red box in (a).

Following the fabrication of the bottom cavity layers, SWCNT films were deposited either by spin coating or vacuum filtration. A critical consideration in constructing microcavities incorporating SWCNT films is the thermal annealing process, which must be tailored to the deposition method due to the sensitivity of film morphology and optical properties to thermal treatment. In particular, vacuum-filtered SWCNT films deposited on top of the BCB layer require a pre-annealing step to ensure mechanical stability and adhesion. A reference thickness for such films is approximately 340 nm, obtained using 1 mL of SWCNT dispersion with a PFO-BPy concentration of 1 mg/mL and a UV-vis S_{22} absorbance value of 1.3477. The film thickness can be tuned by varying the amount of dispersion used during filtration. In contrast, spin-coated SWCNT films do not require additional annealing, as the deposition process itself typically results in sufficient

Table 6.4: List of parameters for fabricating the planar cavity.

Buffer Layer		Gold mirror			DBR mirror		
		Al ₂ O ₃	BCB + PMMA	BCB	PECVD	Sputter	Ion e-beam
Mirror	Top	Au	Au	Au	SiO ₂ /SiN _x	SiO ₂ /TiO ₂	SiO ₂ /TiO ₂
	Bottom	Au	Au	Au	SiO ₂ /SiN _x	SiO ₂ /TiO ₂	SiO ₂ /TiO ₂
Material	Top	Al ₂ O ₃	PMMA	BCB	SiO ₂	SiO ₂	BCB
	Gain	PFO-BPy-CNT VF		PFO-BPy-CNT VF & Spin coating	PFO-BPy-CNT VF	PFO-BPy-CNT VF	PFO-BPy-CNT VF & Spin coating
	Bottom	Al ₂ O ₃	BCB	BCB	SiO ₂	SiO ₂	BCB
<i>n</i>	<i>n</i> _T	1.4	1.47	1.48	1.48	1.48	1.48
	<i>n</i> _G	2	2	2	2	2	2
	<i>n</i> _B	1.48	1.48	1.48	1.48	1.48	1.48
Remark		Al ₂ O ₃ grown by INTLVAC Not accurate	PMMA not good transmission in NIR	Doable Q ~ 28	DBR requires more than 30-pair (Cracked) Q ~ 900	AJA-sputter Long time deposition	DBR from Helia 16-pair Q ~ 1000 High temp.

film uniformity and adhesion. For these films, a typical thickness is approximately 50 nm, using a **PFO-BPy** concentration of 5 mg/mL with the same S_{22} value of 1.3477. Therefore, it is essential to optimize the thermal treatment protocol based on the specific deposition method employed, in order to preserve both the structural integrity of the cavity and the intrinsic optical properties of the embedded **SWCNTs**.

The cavity performance was evaluated using ellipsometric measurements, which provided quantitative insight into the **Q-factor** of the fabricated structures. As expected, microcavities with Au mirrors exhibited relatively low **Q-factor**, with measured values around 28 due to the intrinsic absorption and limited reflectivity of metal mirrors. In contrast, cavities with **DBR** mirrors exhibited significantly higher **Q-factors**: those fabricated using **PECVD** exceeded 900, while those using SiO₂/TiO₂ multilayers surpassed 1000. These results confirm that **DBR**-based planar microcavities are well-suited for high-performance emission device applications.

Using the described mirror structures, cavity layers, and gain media, complete planar microcavity devices were successfully fabricated. The fabrication parameters and resulting device configurations are summarized in Table 6.4.

6.4 Impact of Surface Roughness on Cavity Quality factor

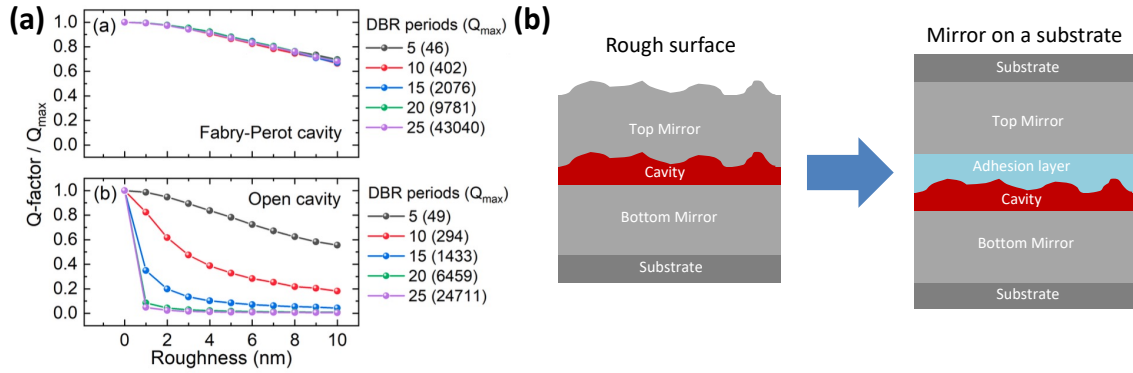


Figure 6.7: (a) Variation of the Q -factor as a function of surface roughness adapted from [172]. (b) Proposed solution for rough-surface cavities: flipping and transferring the existing DBR onto a substrate.

Despite these promising results in the previous section, the fabrication process revealed an unexpected challenge that significantly influenced the Q -factor of the planar microcavities. Specifically, we observed that increasing the thickness of the SWCNT layer led to a notable degradation in surface smoothness. Our chosen substrates (e.g. fused silica) are polished to guarantee surface roughness below 0.5 nm, and the subsequently deposited metal or dielectric films tend to replicate this smoothness. However, due to the nanoscale dimensions of SWCNTs in solution, their inherent tendency to aggregate during deposition processes such as vacuum filtration or spin coating, and the contribution of other materials such as polymer layers, the resulting films exhibit substantially increased surface roughness—often more than an order of magnitude higher than that of the underlying substrate. This excessive roughness significantly compromises the overall smoothness and optical quality of the microcavity structure. A review of relevant literature supports this observation, indicating that surface roughness can severely affect the Q -factor; for instance, a surface roughness of approximately 10 nm has been shown to reduce the Q -factor by nearly 30% in Fig. 6.7(a) [172].

The surface morphology of the DBR layers is influenced by the deposition method. Among the techniques considered, sputtering and e-beam evaporation generally produce smoother surfaces compared to PECVD, as supported by prior study [14]. However, spin-coated films SWCNT typically introduce significant surface roughness illus-

trated in the left image of Fig. 6.7(b). When a DBR stack is deposited directly onto such a rough film, the surface irregularities propagate into the multilayer structure. Thus, the top DBR carries the surface topography of the SWCNT-film underneath. This not only lowers the reflectance of the DBR but also leads to a substantial decline in the Q-factor of the resulting microcavity.

To mitigate this problem, we adopted an alternative fabrication approach. Instead of depositing the DBR directly on top of the SWCNT layer, we first fabricated the DBR structure on a separate substrate. The DBR was then flipped and transferred onto the pre-coated SWCNT film using an adhesion layer. This method minimizes surface roughness propagation into the DBR stack and preserves its high reflectance, ultimately enabling the fabrication of microcavity devices with improved Q-factors (Fig. 6.7(b)).

Based on the fabrication results of planar microcavities employing both metallic and dielectric mirrors, the following chapter will present a detailed discussion on their optical characterization.

Chapter 7

Single-Walled Carbon Nanotube Emission in the Strong and Weak Coupling Regimes

The previous chapters discussed the individual components of [SWCNT](#) film embedded-microcavity devices: a protocol for preparing high-quality [SWCNT](#) thin films and their experimental characterization results (Chapter 5), and the design and successful fabrication of dielectric mirrors, empty microcavities, and microcavities integrated with [SWCNT](#) thin films (Chapter 6). This chapter presents the optical measurement results obtained from the planar microcavity samples described in the preceding chapter.

7.1 Optical Spectroscopy Setup

The optical properties of [SWCNTs](#), planar microcavities, and their integrated [SWCNT](#)-cavity systems are characterized using a range of various spectroscopy techniques. The absorption and emission behaviors of [SWCNTs](#) in solutions and films on substrates have been extensively studied. First, absorption measurements are relatively straightforward and can be performed using commercially available UV-Vis spectrophotometers equipped with broadband tungsten or xenon light sources. These instruments measure the transmittance of light through the sample in a fixed path length (typically 1 cm) cuvette and subsequently calculate the absorbance spectrum. While not identical to true absorption spectra, the resulting data provide closely related and insightful information about the underlying optical transitions and electronic band structures. Due to

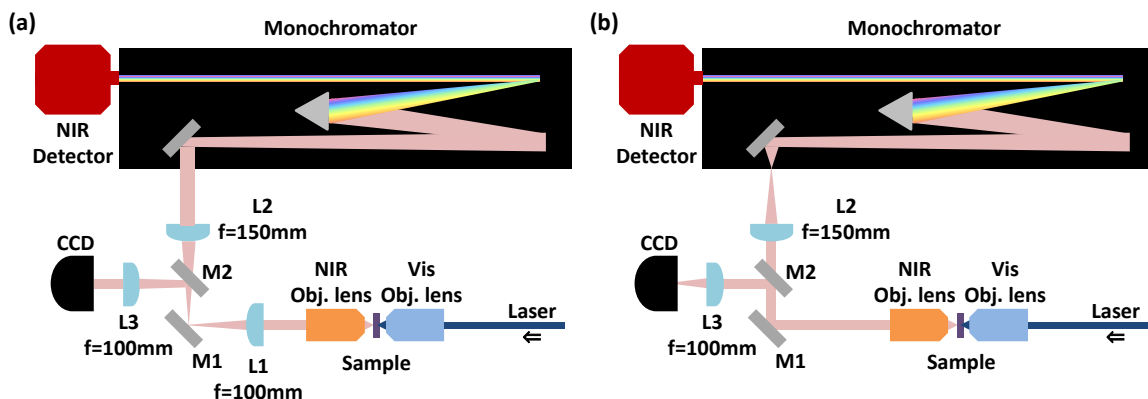


Figure 7.1: Optical setup for PL measurements in (a) far-field imaging and (b) near-field imaging configurations.

the quasi-1D nature of SWCNT discussed in Chapter 3, van Hove singularities appear in the density of states, leading to well-defined optical transitions that are highly dependent on tube diameter and chirality. Among these, optical transitions in the visible and NIR ranges are of particular interest.

For semiconducting SWCNTs, the lowest energy optical transition is labelled S_{11} , whereas higher-order transitions (e.g., S_{22}) occur at shorter wavelengths. In this study, we focus on (6,5) chirality SWCNT, where the S_{11} transition appears near 1010 nm in the NIR, and the S_{22} transition occurs around 575 nm in the visible range at room temperature. We employ an excitation scheme targeting the S_{22} transition and collect the resulting PL emitted from the S_{11} transition. Consequently, the optical setup must accommodate both visible-wavelength components for excitation and NIR-compatible optics for efficient detection of the emitted signal.

Photoluminescence Spectroscopy Setup

Instead of using a commercial spectrometer, we developed a customized absorption PL spectroscopy setup with a 2D charge-coupled device (CCD). This full 2D detection configuration enables the simultaneous collection of both direction information (for example, energy and space) across a large field of view in a single exposure, offering enhanced data throughput and flexibility for complex samples. Compared to 1D optical measurements, 2D imaging techniques provide several significant advantages.

First, 2D imaging captures spatial information across both the x and y directions, so-called **near-field (NF)** imaging, enabling visualization of non-uniformities, defects, and mode profiles at once. In contrast, such comprehensive information would require a time-consuming accumulation of multiple **1D** line scans taken at different spatial positions. Additionally, in angle-resolved measurements enabled by Fourier optics, **2D** detectors allow the simultaneous acquisition of momentum space data along both k_x and k_y , which is known to be **far-field (FF)** imaging. The **FF** spectroscopy is crucial to measure the energy-momentum relation, effectively mapping the electronic band structures of the system. This **2D** imaging can reveal detailed mode structures and intensity distributions in microcavities or waveguides, providing critical insights into confinement and coupling behavior, offering a complete picture of polariton dispersion and anisotropy. With the integration of polarization optics or interferometry, **2D** detection systems can further extend to polarization- and phase-resolved imaging, unlocking even richer optical information about the underlying photonic and excitonic properties.

Our custom-built **2D** spectroscopy system is set to characterize both planar microcavity devices and **SWCNT** films, whose diagrams are drawn in Fig. 7.1 and in Fig. 7.2, for the optical configurations used for **PL** and transmission measurements, and for white light reflectance, respectively. Given the S_{22} absorption (visible) and S_{11} emission (**NIR**) characteristics of (6,5) **SWCNTs**, the optical components in the setup were categorized into three parts: (1) the input section, (2) the excitation pump laser section, and (3) the output section where the signal is collected from the sample. Figure 7.1(a) illustrates the setup used to measure the **PL** transmission spectra of the prepared samples. One of the standard optical characterizations involves performing power-dependent **PL** measurements. To optimize the excitation power density within the available maximum laser output power, a visible-range objective lens was placed in front of the sample to tightly focus the pump laser beam. A 575 nm laser, which lies in the S_{22} optical transition of (6,5)-**SWCNTs**, was chosen to maximize the **PL** output from the **SWCNT**, based on the results of **2D PL** maps obtained from both liquid- and film-phase measurements. For this purpose, a tunable laser (C-WAVE-Vis, HÜBNER Photonics GmbH), covering the 450–650 nm range, was employed. The laser beam entered from the lower right side in the schematic and was focused onto the sample via a visible-range objective lens. The excitation laser beam diameter was determined to be 56.7 μm , assuming a Gaussian beam profile and measured via the knife-edge method. With an incident laser power of 1 mW, this corresponds to an estimated power density of approximately $4 \times 10^7 \text{ } \mu\text{W cm}^{-2}$ at the sample surface.

To collect the S_{11} **NIR** emission from the sample, an Olympus LCPlan N 100 $\times$ IR objective lens (NA = 0.85) was used. Despite its short working distance (1–2 mm),

the high numerical aperture allows for signal collection over a broad angular range of approximately 120° . The collected emission was passed through two lenses, L1 and L2, which together enabled FF imaging. Specifically, L1 focused the signal at the back focal plane of the objective lens, and L2 converted it into the Fourier plane, directing the beam to the detector. The momentum space axis, $k_{||}$, was calibrated using custom-fabricated square lattice patterns with lattice constants ranging from $2\text{ }\mu\text{m}$ to $20\text{ }\mu\text{m}$, an approach inspired by Kim *et al.* [118]. FF images of these lattices were acquired, and the positions of the diffraction spots were fitted to determine the corresponding momentum values. This calibration enabled the precise mapping of the $k_{||}$ axis for the 2D angle-resolved PL images. Due to spatial constraints, a gold-coated mirror (M1) was incorporated to steer the beam path while minimizing optical losses, ensuring uniform signal collection across a wide NIR range. The focal lengths of L1 and L2 were set to 100 mm and 150 mm, respectively, yielding a $1.5\times$ image magnification.

The spectrally dispersed signal was analyzed using a monochromator (HRS-750, Teledyne Vision Solutions) equipped with a 600 grooves/mm grating blazed at $1.0\text{ }\mu\text{m}$, and subsequently detected using a 2D InGaAs detector array (NIRvana, Teledyne Vision Solutions). For optical path alignment and real-time monitoring during measurements, an OMAX 5M CCD camera was positioned in front of the monochromator, with a flip mirror (M2) allowing toggling between spectral detection and imaging modes.

For NF imaging, the configuration remained identical to the FF imaging setup except that the L1 lens was removed. This allowed the collimated signal collected by the NIR objective lens to be directly relayed to the detector through L2, as shown in Fig. 7.1(b). With the NIR objective lens having a focal length of 1.8 mm and L2 set to 150 mm, the total system magnification was approximately $88.3\times$, verified using USAF 1951 Glass Slide Resolution Targets.

Absorption Spectroscopy Setup

Absorption spectra were acquired using either reflection or transmission configurations. In this study, we adopted the former. The reflection measurement setup was implemented by integrating a broadband white light source and a non-polarizing beam splitter (NPBS) into the existing 2D PL imaging system. Broad-spectrum illumination from a halogen lamp was directed onto the sample, and the reflected signal in the NIR spectral region was selectively collected for analysis. This configuration enabled spectral reflectance measurements without significant modification to the optical path of the PL system. Similar to the 2D PL imaging setup, both FF and NF reflection mea-

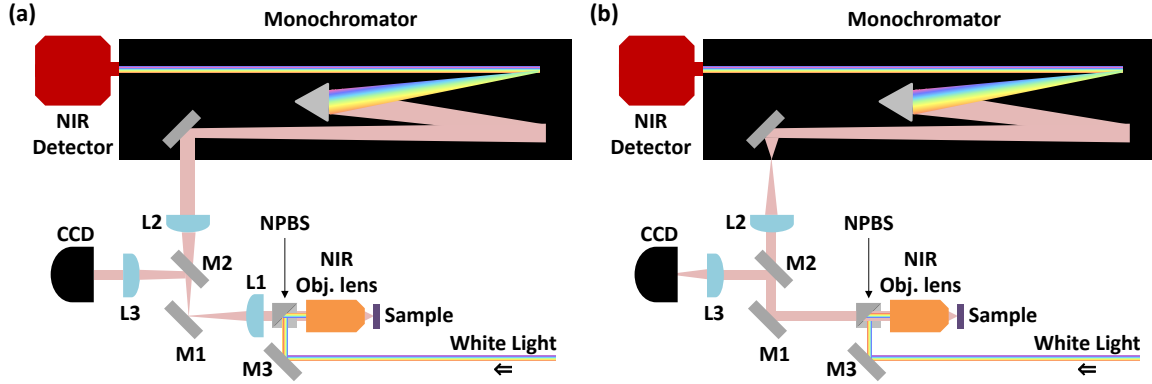


Figure 7.2: Optical setup for reflection measurements in (a) far-field imaging and (b) near-field imaging configurations.

measurements could be performed, depending on whether the removable L1 lens was in place, as shown in Fig. 7.2(a) and Fig. 7.2(b), respectively. Note that we calibrated the optical path with the same white light source in the absence of the sample, with which we obtained the absorption spectra.

7.2 Planar Microcavities for Exciton-Polaritons in Single-Walled Carbon Nanotubes

As discussed in the previous chapter, various types of mirrors were fabricated and examined. In this section, we compare the results obtained from several representative combinations used to fabricate exciton-polariton devices.

7.2.1 Mirror Combination: Au-Au

First, we investigated a planar microcavity structure consisting of both top and bottom Au mirrors, with complete layer information provided in the leftmost panel of Fig. 7.3 to investigate exciton-polariton formation in SWCNTs resulting from the strong light-matter coupling. This configuration has been previously reported in the literature; our objective was to assess the reproducibility of such results using our in-house fabrication process.

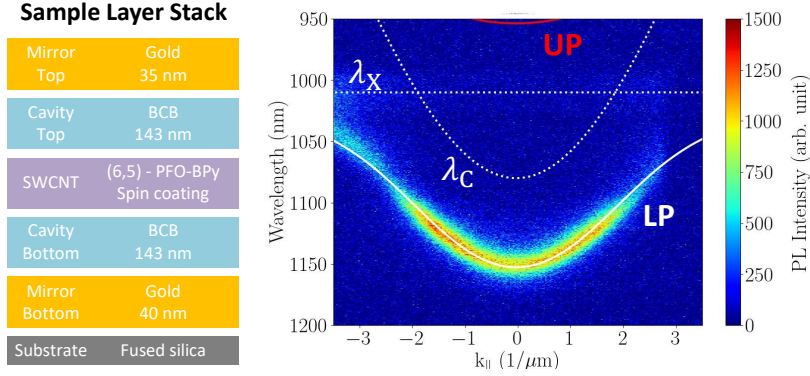


Figure 7.3: Schematic of a planar microcavity consisting of both Au top and bottom mirrors (left), along with the corresponding angle-resolved PL 2D data (right).

To facilitate transmission-based optical characterization, the SWCNT-microcavity device was constructed on a transparent fused silica substrate. A 40 nm-thick bottom Au mirror was deposited via electron-beam evaporation. The cavity layer, with a total thickness of 143 nm, was formed using BCB polymer, in which SWCNTs were embedded at the center by sequential spin-coating. Specifically, a bottom BCB layer was spin-coated first, followed by deposition of the SWCNT layer about 50 nm thick, and finally a top BCB layer was added to complete the cavity structure. A 35 nm-thick top Au mirror was subsequently deposited to enclose the cavity.

Angle-resolved PL measurements, shown on the middle panel of Fig. 7.3, reveal the LP dispersion. For comparison, reflection measurements were performed on a corresponding cold cavity device, identical in structure but without the embedded gain medium (SWCNTs), using a broadband white light source. From these measurements, the bare cavity mode (at 1080 nm, indicated by a quadratic dotted line) and the exciton resonance (depicted as a horizontal dotted line) were identified. Using these modes, the polariton branches were obtained by fitting: the LP branch (white solid line) and the UP branch (red solid line). From this fitting, a VRS of 210 meV was extracted, confirming strong light-matter coupling in the system. As shown in the right panel of Fig. 7.3, the device is red-detuned, with a measured detuning of -79.6 meV. The low Q-factor results in a broad LP emission linewidth, measured to be 18.1 meV.

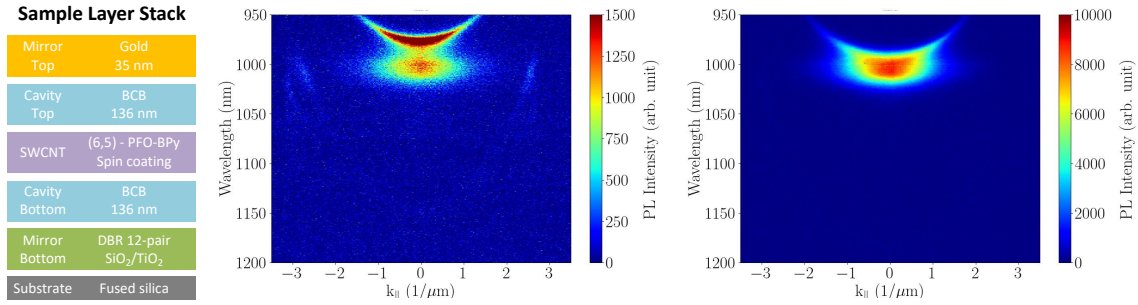


Figure 7.4: Schematic of a planar microcavity consisting of Au top mirror and bottom DBR mirror (left), along with the corresponding angle-resolved PL 2D data acquired at different positions (middle and right).

7.2.2 Mirror Combination: DBR-Au

The next structure under investigation was a hybrid microcavity comprising a bottom DBR formed by 12 pairs of SiO₂-TiO₂ layers, and a top mirror consisting of a 35 nm-thick Au film shown in the left panel of Fig. 7.4. The cavity layer was fabricated by spin-coating BCB layers of 136 nm thickness on both the bottom and top, with the approximately 50 nm SWCNT gain medium embedded centrally between these layers. This sample exhibited a blue detuning characterized by the detuning value of $\Delta = 12.3$ meV, where the cavity resonance wavelength $\lambda_C = 1000$ nm and the exciton wavelength $\lambda_X = 1010$ nm. In comparison to the metal-metal device, the DBR-metal device shows a small blue detuning, which is attributed to the reduced cavity thickness relative to the Au-Au microcavity. From fitting the dispersion, a VRS of 30 meV was extracted.

Figure 7.4 presents two angle-resolved 2D PL datasets acquired at different positions within the same device. In the left optical plot, a parabolic dispersion consistent with the UP branch is clearly observed, accompanied by a bright spectral feature below it, attributed to the LP branch. This behavior is interpreted as a result of blue detuning and an upconversion process. Amin *et al.* [13] reported similar phenomena in CdSe nanoplatelet polariton systems, where energy upconversion was observed once the system achieved a high Q-factor (~ 300). The reduced photon loss in such cavities enables efficient population transfer from dark states to the UP branch. In our case, excitation at LP energies leads to PL emission from the UP branch, indicating phonon-mediated population exchange. We speculate that some upconversion process may enhance UP emission, which requires further investigation. The device under investigation utilizes

a hybrid mirror configuration of DBR and Au, resulting in a Q -factor of approximately 127, about five times greater than that of devices with Au-Au mirror configurations. This higher Q -factor leads to longer photon lifetimes, allowing more time for population of the UP state prior to photon escape. Additionally, vibrational coupling facilitates the involvement of quasi-dark states in mediating population transfer. In contrast, the right panel displays a more prominent LP branch compared to the left, although its polaritonic origin remains unclear. The observed spectral features lie in the intermediate regime between weak and strong coupling. Despite the Q -factor exceeding 100, higher than in devices with Au-based mirrors, strong light-matter coupling appears to be suppressed, potentially due to unknown extrinsic or intrinsic limiting factors. This behavior is observed in devices employing a DBR-DBR mirror configuration, which otherwise provides a higher Q -factor. Collectively, these results indicate that under the current experimental conditions, strong exciton-photon coupling is not consistently achieved throughout the sample.

7.2.3 Mirror Combination: DBR-DBR

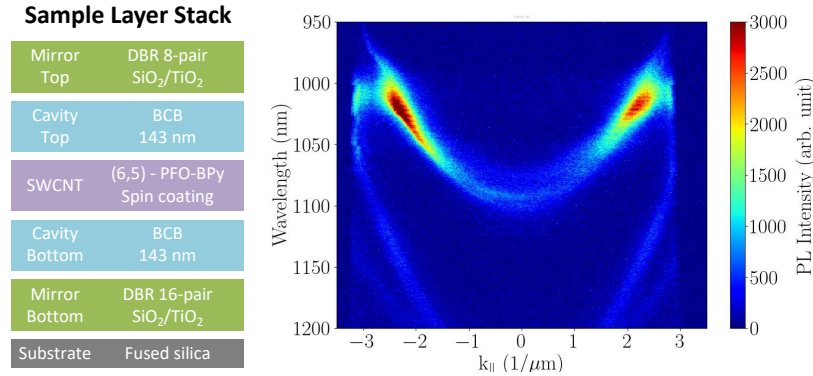


Figure 7.5: Schematic of a planar microcavity consisting of both DBR top and bottom mirrors (left), along with the corresponding angle-resolved PL 2D data (right).

The last structure investigated was a DBR-DBR microcavity, which exhibited a Q -factor of approximately 274, about twice as high as that of the DBR-Au configuration and an order of magnitude higher than that of the Au-Au mirror structure. Consistent with the previous designs, the cavity layer comprised two BCB layers with a thickness of 143 nm. The DBR mirrors consisted of alternating SiO_2 and TiO_2 layers, with 12

pairs forming the bottom mirror and 8 pairs composing the top mirror. This intentional asymmetry in the number of pairs was deliberately introduced to drive most signal leakage through the top DBR mirror; when the reflectivities of the top and bottom mirrors are identical, emission occurs with equal probability in both directions, thereby diminishing the PL intensity collected from the top and resulting in a weak signal that is challenging to detect.

The 2D PL data obtained from this sample identify the cavity and exciton resonances at 1080 nm and 1010 nm, respectively, which is consistent with the first Au-Au microcavity structure. However, the LP emission intensity at $k_{\parallel} = 0$ is markedly reduced, appearing nearly negligible. The extracted VRS is approximately 80 meV, which is less than half the value observed in the Au-Au device, although the cavity mode (at 1080 nm) and detuning ($\Delta = -79.6$) are similar. PL intensity is observed near finite in-plane wavevectors ($k_{\parallel} \sim 2(1/\mu m)$), indicating polariton accumulation at a bottleneck, which inhibits efficient scattering down to $k_{\parallel} = 0$.

Comparing the three microcavity configurations, the Au-Au structure distinctly demonstrates strong exciton-photon coupling (the largest VRS of 210 meV), as evidenced by the well-resolved LP dispersion. In contrast, we interpret that the DBR-Au hybrid cavity appears to reside in a transitional regime, wherein strong coupling is not fully established and the LP branch remains incompletely formed. The DBR-DBR configuration, which shares structural similarity with the Au-Au device aside from the mirror composition and possesses comparable detuning, exhibits a pronounced bottleneck effect characterized by exciton accumulation and an almost negligible PL signal at $k_{\parallel} = 0$. This phenomenon is attributed to the increased PL lifetime induced by the high reflectivity of the DBR mirrors; however, the consequent multiple internal reflections result in significant absorption within the SWCNT layer, thereby impeding effective exciton-polariton interactions. This mechanism likely accounts for the absence of reported exciton-polariton formation and related condensate phenomena in DBR-based microcavity structures embedding SWCNTs.

For exciton-polariton lasing, it is essential to overcome the bottleneck effect typically observed in the red-detuned regime. This can be addressed by fabricating devices with shorter cavity layers, which blue-shift the cavity dispersion. As a result, we anticipate that the exciton-polariton detuning values approach zero or become blue-detuned, thereby facilitating more efficient polariton relaxation and population at the bottom of the LP branch. Since our CW laser source has a limited maximum power (~ 90 mW), we need to examine strategies for lowering the condensation threshold to enable observation of exciton-polariton condensation within the available laser pump power range.

7.3 Photon Lasing in Single-Walled Carbon Nanotube Films

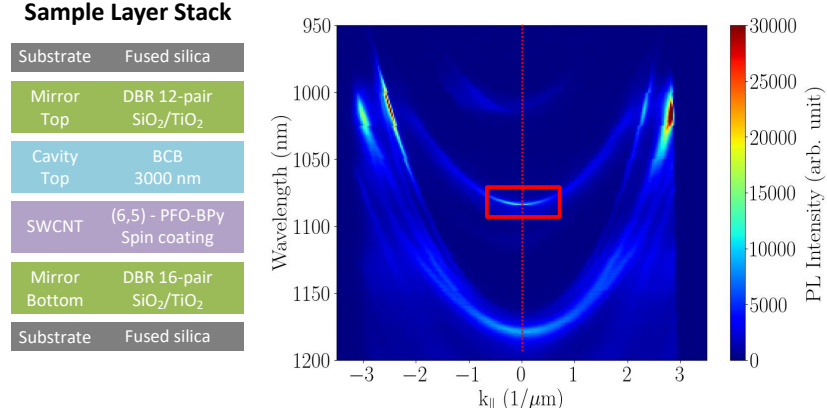


Figure 7.6: Schematic of the photon lasing device structure and PL measurements of the photon lasing sample: angle-resolved 2D plot at a pump power of 90 mW.

The comparative analysis of the three mirror-based microcavity structures in the previous section underscores the importance of the overall device *Q-factor*, detuning values to match the cavity photon and the exciton resonances, and gain media emission properties. And the strong optical absorption of SWCNTs [222], combined with EEA [102], significantly impedes efficient exciton–polariton interactions, particularly in scenarios involving high mirror reflectivity or prolonged exciton generation. To address these limitations, a revised cavity architecture was implemented in which the SWCNT film was repositioned from the center of the cavity layer to a location directly above the substrate, thereby reducing its spatial overlap with the cavity’s standing wave field.

In addition, the cavity thickness was increased to 4400 nm (an approximately 50 nm-thick SWCNT film and a 3000 nm-thick BCB layer were deposited, with an air gap formed due to the presence of foreign material) to enlarge the optical mode volume, which is evaluated based on the presence of two cavity modes within the stopband, ranging from 900 nm to 1170 nm. These cavity modes, located around 1010 nm and 1080 nm, are clearly observed in the 2D PL map shown in Fig. 7.6, as well as in the corresponding 1D spectrum presented in Fig. 7.7. The increased thickness allows multiple longitudinal modes to exist within the stopband, thereby enabling better spectral overlap and coupling with the excitonic gain spectrum. As a result, this structure enhances the emission collection efficiency by leveraging the sharp cavity modes. To avoid degradation of the *Q-factor* due to surface roughness of the SWCNT film, a pla-

nar microcavity was fabricated by capping a pre-grown DBR mirror onto a fused silica substrate. This structural design aimed to operate in the weak light–matter coupling regime while maintaining a high Q-factor of approximately 1000 to enable photon lasing. Photon lasing was successfully observed under this configuration.

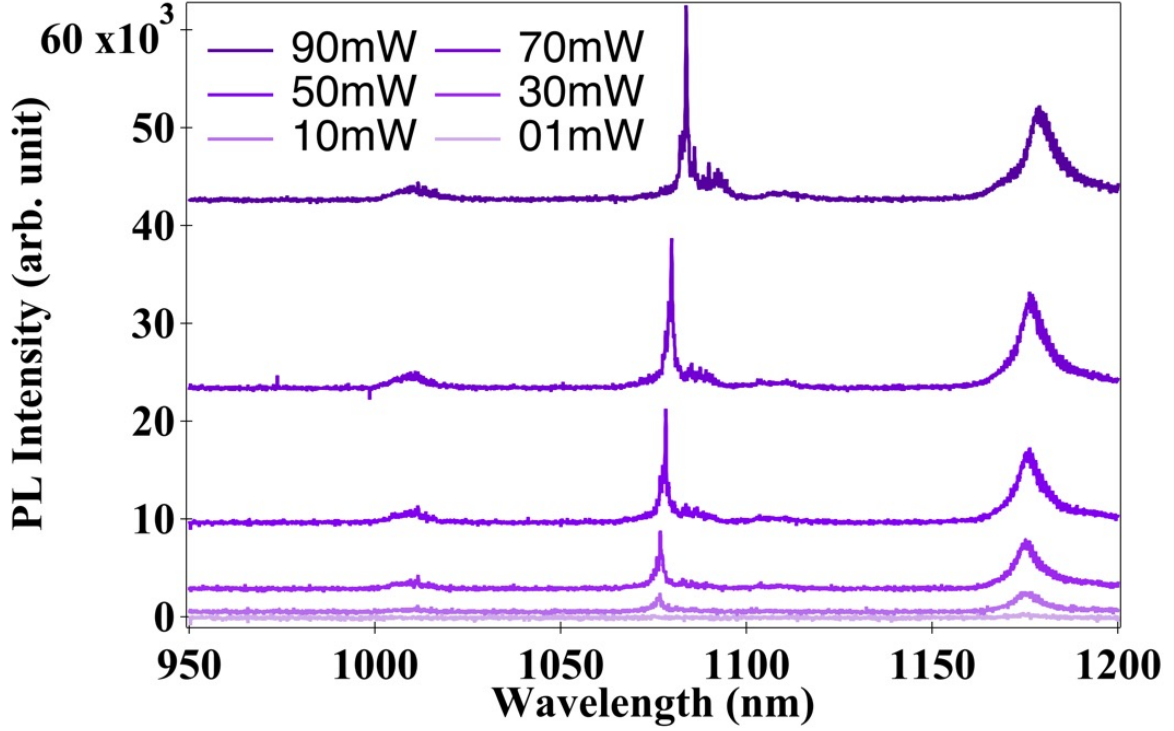


Figure 7.7: Extracted 1D PL intensity at $k_{||} = 0$ as a function of pump power from 1 mW to 90 mW from angle-resolved 2D plot. (vertically offset plots)

Figure 7.6 presents a schematic of the cavity design along with angle-resolved 2D PL data acquired at a pump power of 90 mW. The 1D PL spectrum at $k_{||} = 0$ was extracted by sampling along the vertical red dashed line indicated in the 2D maps. The spectral region corresponding to the red box highlights the onset of photon lasing. 2D angle-resolved PL measurements were performed under varying pump powers ranging from 1 mW to 90 mW. For each excitation condition, the corresponding 1D PL spectrum at $k_{||} = 0$ was extracted. These spectra were compiled into a single panel to facilitate comparison of the power-dependent emission characteristics (Figure 7.7).

Based on the data obtained from the figure, the spectra corresponding to the lasing regime were analyzed and fitted to extract the linewidth, peak photoluminescence

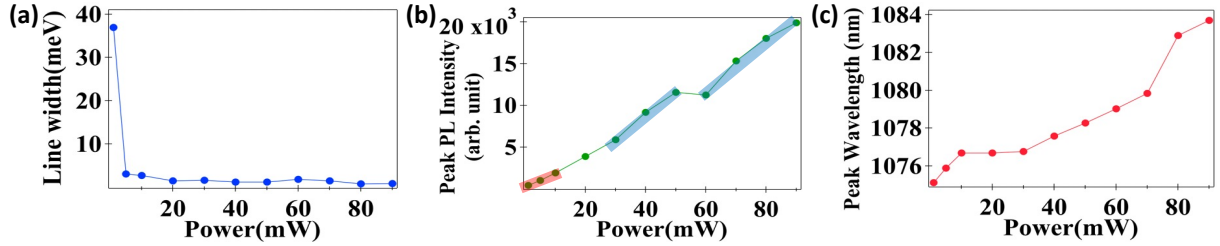


Figure 7.8: Evolution of lasing characteristics with pump power for the photon lasing sample: (a) emission linewidth, (b) peak PL intensity with slope guideline below 20 mW (red) and above 20 mW (blue), and (c) peak wavelength.

intensity, and peak emission wavelength as functions of the input pump power (Figure 7.8). These results provide evidence for the occurrence of photon lasing in this cavity structure.

The first and most compelling evidence is observed in the spectral linewidth, as clearly shown in Fig. 7.8(a). The linewidths were extracted from one-dimensional spectral slices near 1080 nm in the power-dependent 2D map shown in Fig. 7.7, using Lorentzian fitting of the narrow emission peaks. A sharp reduction in linewidth is observed starting from a pump power of 5 mW. At this power, the linewidth is approximately 3.1 meV, which narrows to around 2.7 meV at 10 mW, and further decreases to the range of 1.1 meV to 1.5 meV, remaining relatively constant even as the pump power increases beyond 20 mW. In Fig. 7.8(b), which displays the peak PL intensity, no prominent nonlinear behavior is apparent in the conventional power-dependent curve. This is likely due to the limited signal intensity at pump powers below 1 mW, which falls below the detection threshold and therefore is not shown in the graph. Nonetheless, when the power range is divided into regions below and above 20 mW, and the slope in each regime is evaluated (excluding the outlier at 60 mW), a nonlinear increase in intensity is evident below 20 mW, followed by a clear linear trend above this threshold. Meanwhile, the pump laser used was a continuous-wave (CW) source at 575 nm, which continuously irradiates the sample and induces thermal effects. As shown in Fig. 7.8(c), this leads to a noticeable redshift in the emission peak wavelength, confirming the presence of heating effects associated with CW excitation.

Another sample with a thicker cavity was examined to investigate the threshold power. This device features a structure similar to the previous one but with an increased cavity thickness of approximately 15.4 μm , resulting from a 400 nm-thick SWCNT film and a 4000 nm-thick BCB layer. In addition to this structure, a significant air gap was

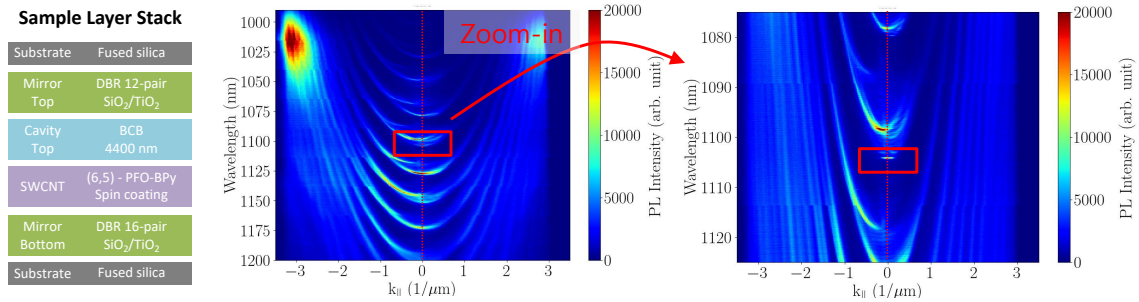


Figure 7.9: Schematic of another photon lasing device structure and PL measurements of the photon lasing sample: angle-resolved 2D plot at a pump power of 59 mW. A zoomed-out view of the 2D PL data is shown in the center, while a zoomed-in view is presented on the right.

observed, primarily due to edge effects. As with the previous device, the top DBR transfer method is susceptible to contamination by foreign materials, which can introduce undetectable air gaps. Furthermore, this sample exhibits an additional air gap, approximately $10 \mu\text{m}$ in size, attributed to spin-coating edge effects. Due to the increased cavity thickness compared to the previous device, multiple cavity modes were observed in the 2D PL map. A magnified view of the region of interest is shown in Fig. 7.9.

As with the previously analyzed sample, 1D PL spectra at $k_{||} = 0$ were collected under varying pump powers up to 59 mW, as shown in the upper inset of Fig. 7.10(a). However, unlike the earlier case, the 2D PL map reveals the presence of multiple competing modes, which obscure a clearly defined emission peak at the central wavelength. The region of interest is highlighted by the red-dotted box, which is magnified and displayed in the bottom panel of Fig. 7.10(a). In this region, the lowest-energy emission mode initially appears at approximately 1101 nm when the pump power is 1 mW. As the excitation power increases, the emission peak undergoes a gradual redshift. This redshift behavior is consistent with thermal effects.

A more detailed analysis of the lasing characteristics is presented in Fig. 7.10(b). The upper panel shows both the integrated peak PL intensity and emission linewidth as functions of pump power. A distinct threshold behavior is observed around 20 mW, beyond which the PL intensity increases abruptly with a slope approximately 1.8 times greater than that observed below the threshold. Simultaneously, the emission linewidth narrows significantly near this threshold, which is a typical signature of the onset of stimulated emission. The bottom panel of Fig. 7.10(b) further confirms the redshift of the peak wavelength with increasing pump power, again suggesting thermal effects.

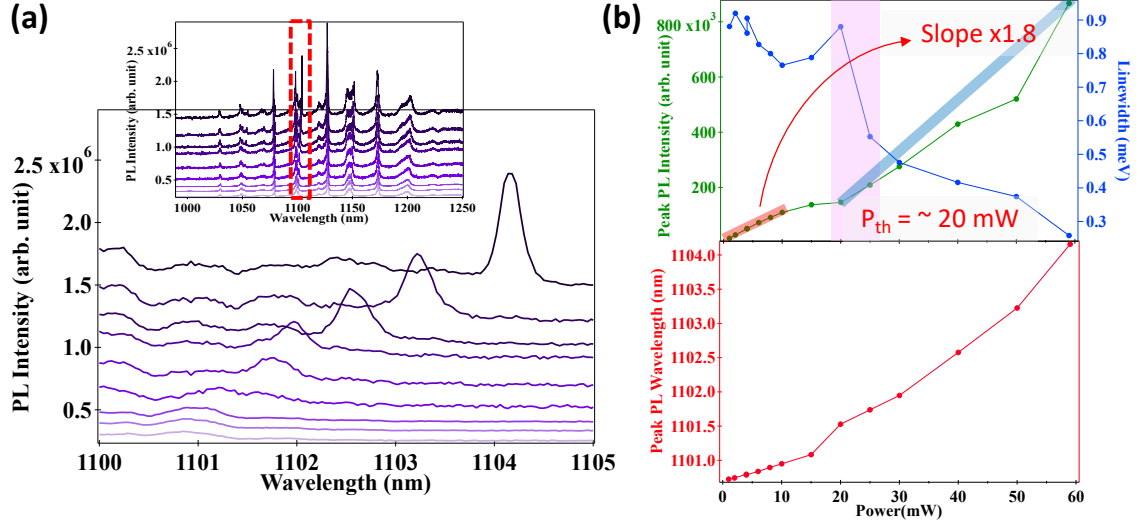


Figure 7.10: (a) Pump power-dependent 1D PL intensity extracted at $k_{\parallel} = 0$ from angle-resolved 2D data. The plots show the extracted intensity as a function of pump power, ranging from 1 mW to 59 mW. The upper inset displays the full measurement range, while the red-dotted region is magnified and presented in the lower panel for detailed analysis. (b) Evolution of lasing characteristics with increasing pump power for the photon lasing sample. The upper panel shows the emission linewidth and peak PL intensity as functions of pump power, with slope guidelines indicated in red (below 20 mW) and blue (above 20 mW). The lower panel presents the corresponding peak emission wavelength.

However, the absence of linewidth broadening above the threshold, despite the thermal redshift, indicates that the emission arises from a lasing process rather than purely thermal population effects. This decoupling of linewidth narrowing from thermal broadening serves as additional evidence of coherent light amplification in the system.

To further elucidate the lasing phenomenon, a comparison of three spectra, absorbance, film PL, and DBR-integrated PL with the first sample, was conducted, as shown in Fig. 7.11. In the absence of the DBR cavity, the emission appears at approximately 1010 nm, which is slightly red-shifted (about 10 nm) from the absorbance peak located at 1000 nm. Although the absorbance at 1010 nm is approximately 60% of the peak value, this region still retains significant oscillator strength due to the highly localized excitonic nature of SWCNTs.

However, when photons around 1010 nm are repeatedly reflected within the cav-

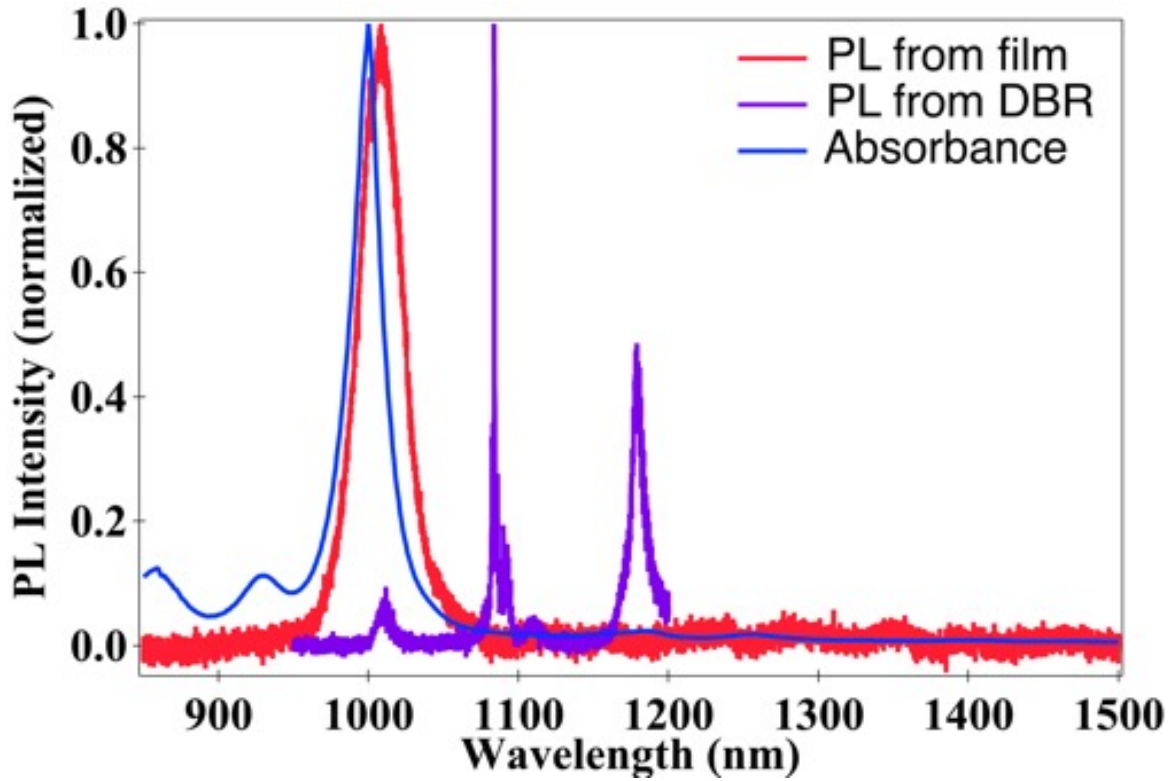


Figure 7.11: Normalized absorbance spectrum, PL from the SWCNT film, and PL from the first DBR sample.

ity as a result of the DBR mirrors, they strongly interact with the embedded SWCNTs. While this enhances the light-matter coupling, it also leads to increased reabsorption, thereby hindering the sustained photon accumulation required for achieving population inversion.

In contrast, when the cavity mode is tuned to approximately 1080 nm, near the tail end of the absorption spectrum, the lasing condition becomes more favorable. In this spectral region, reabsorption is significantly reduced, and the photoluminescence peak overlaps with the high-Q-factor cavity mode. This spectral alignment facilitates the establishment of population inversion and the onset of stimulated emission, strongly indicating that lasing is enabled by the optimized spectral overlap and minimized reabsorption losses at 1080 nm.

Chapter 8

Conclusion

8.1 Summary of Contributions

The pursuit of novel coherent light sources has increasingly turned to low-dimensional materials, whose strong excitonic effects are stable even at room temperature, and tunable optical properties offer exciting opportunities for nanoscale photonics. Among these, semiconducting SWCNTs stand out owing to their direct bandgap and efficient NIR emission. However, achieving lasing from SWCNT-based systems is sought-after due to intrinsic losses and nonlinear processes. This thesis presents the first experimental realization of photon lasing from SWCNT thin films embedded in planar microcavities with dielectric DBR. By systematically exploring light–matter interactions across both strong and weak coupling regimes, this work advances our understanding of excitonic and photonic behavior in carbon-based nanostructures under photonic confinement.

The successful design and fabrication of high-reflectivity DBR cavities, coupled with the integration of well-dispersed and optically active SWCNT films, enabled coherent light emission through optical pumping. This achievement represents a key milestone in the development of SWCNT-based photonic devices and paves the way for future studies of nanocarbon optoelectronics.

Key contributions and findings of this work include:

- Achieving the high-purity SWCNT solutions and a comparative analysis of two distinct SWCNT sorting methods using ATPE and conjugated polymer-based dis-

persion (PFO-BPy), highlighting differences in chirality purity and optical performance.

- Identification of the mechanisms behind PL degradation under repeated measurements and thermal annealing, emphasizing the sensitivity of SWCNT films to processing history.
- Design of high Q-factor microcavities through transfer matrix calculations and fabrication of the designed structures. Comparison study of experimental results and theoretical values.
- Development of a DBR transfer technique using an upside-down lamination approach to cap pre-grown DBR, which minimizes surface roughness effects caused by the underlying SWCNT films and improves the cavity Q-factor.
- Design and implementation of a custom optical setup for NIR PL and absorption spectroscopy setup.
- Systematic investigation of photonic behavior in microcavities with three different mirror configurations, elucidating the relationship between cavity structure and light–matter coupling regime and optical measurement results.
- Observation of photon lasing under weak coupling conditions, characterized by spectral narrowing and nonlinear emission behavior.

8.2 Limitations and Challenges

Despite these achievements, several challenges remain. One of the foremost challenges is achieving uniform SWCNT film morphology. It requires careful design optimization and reproducible fabrication of SWCNT dispersion quality in solvents, as well as precise control over film thickness and surface roughness. Optimization of the overall device fabrication process is essential to enhance PL intensity and maintain spectral purity. Moreover, the short lifetime of polaritons and the presence of non-radiative loss channels limit the realization of exciton–polariton condensation.

While the exciton-polariton energy dispersions were clearly observed, exciton-polariton lasing has not achieved yet. A primary limiting factor is the intrinsic material property whereby the close overlap between absorption and emission spectra leads to strong re-absorption, significantly reducing the probability of radiative emission necessary for

polariton lasing. A promising approach to mitigate this issue is to spectrally separate the absorption and emission peaks. Functionalization of SWCNTs or the introduction of controlled defects in SWCNTs can create exciton traps that emit at red-shifted wavelengths relative to the absorption spectrum, thereby significantly reducing re-absorption losses. Subsequently, the center wavelength of the microcavity can be redesigned to couple effectively with these new shifted exciton resonances, optimizing light-matter interactions.

All of our polymer-wrapped SWCNT films, prepared by vacuum filtration and spin coatings, show random orientations of SWCNT films even with > 99.9%-pure (6,5) SWCNTs. This randomness arises from variations in nanotube lengths and the presence of polymer-wrapped surfaces, which hinder uniform alignment during film formation. These randomly oriented networks are far from ideal, as the junctions between misaligned nanotubes often act as non-radiative recombination centers and add unfavorable scattering pathways, both of which suppress radiative relaxation and degrade emission efficiency. Therefore, accurate control of SWCNT alignment and dispersion remains a critical factor for ensuring device reproducibility and performance.

While the present results satisfy several of the critical evaluation criteria for lasing phenomena proposed by *Nature Research* [5], notably, clear demonstration of the threshold behavior and linewidth narrowing, along with specification of the operating conditions, some aspects remain unaddressed. In particular, the beam spatial profile, coherent emission, and statistical verification based on multiple samples were not fully examined in this study. These points will require further investigation in future work to provide a more comprehensive validation of the lasing characteristics.

8.3 Future Works

The results presented in this thesis lay a strong foundation for continued exploration in the field of carbon-based nanophotonics. Building on the findings of this thesis, future research directions include:

- Investigating the collective optical behavior and energy structure of SWCNT films to better understand the origin of ensemble PL spectra.
- Optimizing inter-tube spacing within SWCNT films to maximize PL intensity and minimize detrimental EEA and reabsorption effects.

- Exploring methods to suppress [EEA](#) at high excitation densities to improve lasing thresholds and efficiency. (e.g., [SWCNT](#) functionalization)
- Conducting systematic studies to understand the absence of exciton–polariton condensation in [SWCNT](#) systems, despite strong coupling signatures.
- Enhancing fabrication reproducibility to consistently demonstrate photon lasing from [SWCNT](#) films in planar microcavities, while also meeting the *Nature Research* lasing criteria for coherent emission and beam spatial profile.
- Extending the work to other chirality species to investigate wavelength tunability and demonstrate polariton and photon lasing across the near-infrared spectrum.

This research represents a significant step forward in the field of carbon-based photonic device engineering. Through a comprehensive investigation of light-matter interactions in semiconducting [SWCNTs](#) embedded in high-quality planar microcavities, this work has demonstrated the feasibility of realizing coherent light emission from [1D](#) excitonic systems. By integrating fundamental excitonic physics with advanced nanofabrication, precise cavity design, and systematic optical characterization, this thesis advances our understanding of the photophysical processes that govern radiative emission in nanomaterials.

Looking ahead, the strategies and insights established here open exciting possibilities for device optimization through control of chirality, alignment, exciton-photon coupling strength, and integration with hybrid quantum systems. As research continues to push the frontiers of nanophotonics, the contributions of this work provide both a solid foundation and a forward-looking vision for the role of [SWCNTs](#) in the future development of quantum photonic and integrated optoelectronic systems, leveraging the unique properties of [SWCNTs](#).

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APPENDICES

Appendix A

Understanding ATPE: Background, Principles, and Procedure

A.1 Background of ATPE

A.1.1 Motivation

CNTs are synthetic material which consist of Carbon (C), atomic number 6 in Periodic table. As carbon has six (6) electrons, the electron configuration is represented $[\text{He}]2s^22p^2$ [182]. Due to the electron configuration, carbon becomes hybridized forms, sp^x where x is from 1 to 3. Fig. A.1 illustrates with and without hybridization cases of carbon.

Specifically, CNT forms sp^2 hybridization, three sp orbitals connect other carbon atoms by σ bonding and planar structure with the angle 120° , in the end, hexagonal structure is established. This hexagonal structure is shown both graphene and CNTs. CNTs have additional constitution, cylindrical structure rolled up hexagonal plane. Due to the cylindrical structure, CNTs have semiconducting or metallic properties by confined circumferential direction, especially SWCNTs: There are three types of CNTs which is defined by the number of walls, SWCNT and MWCNT, MWCNTs are considered as metallic. The rest $2p_z$ orbital is considered as a bounded electron to calculate the energy band structure calculation of SWCNTs by using tight binding model [234]. Chirality which is noted by n and m is defined according to the diameter size of SWCNTs, metallic is in the case of $n - m = 3k$ and semiconducting is $n - m \neq 3k$ where k is an

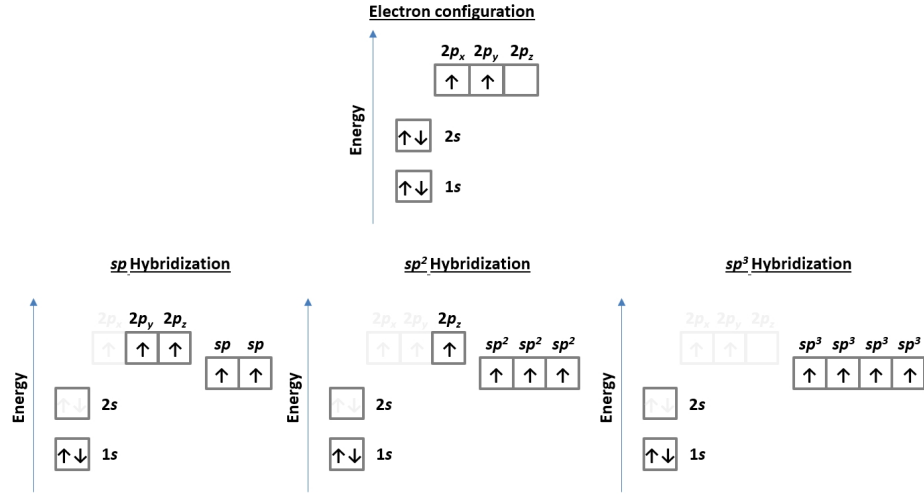


Figure A.1: Kinds of carbon electron configurations [228].

integer. Therefore, SWCNTs have different sizes which are matched with different chiralities and those manifest assorted semiconducting or metallic cases which is power of SWCNTs. This property is only for CNT among carbon allotropes summarized in Table A.1. Other well-known allotropes can be semiconductor, semi-metal, or insulator but CNTs can be both semiconductor or metal, in addition, those have different cases [182].

Dimension	0-D	1-D	2-D	3-D
Allotropes	Fullerene	Carbon Nanotube / Carbyne	Graphene	Diamond
Hybridization	sp^2	sp^2 / sp	sp^2	sp^3
Density [g/cm ³]	1.72	1.2-2.0 / 2.68-3.13	2.26	3.515
Bond length [Å]	1.40 (C=C)	1.44 (C=C)	1.42 (C=C)	1.54 (C-C)
Electronic properties	Semiconductor $E_g=1.9\text{eV}$	Metal or semiconductor	Semi-metal	Insulator $E_g=5.47\text{eV}$

Table A.1: Table of carbon allotropes [228]

Numerous semiconducting and metallic cases of SWCNTs are advantageous to electrical and optical applications because those have different band gap energy or transi-

tion energy. The reason for using the term, transition energy, is metallic also shows absorption spectrum like band gap energy in semiconducting. Fig A.2(a) displays energy diagrams and DOS both cases and Kataura summarized the relation between diameter and transition energies well-known Kataura plot Fig A.2(b) [115]. Further information is in Appendix.

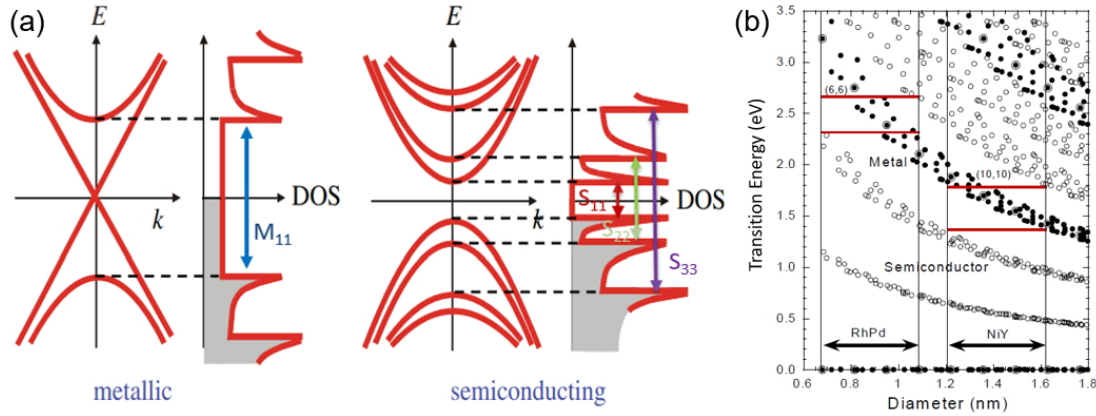


Figure A.2: (a) Energy diagrams and DOS for metallic and semiconducting SWCNTs [72]. (b) The Kataura plot which shows the relations between a diameter of SWCNTs and energy band gap. Open circles are semiconducting, solid circles are metallic, and double circles are armchair metallic SWCNTs [115].

From the calculation results, several materials can be replaced by SWCNTs [228].

- GaP: $E_g = 2.26 \text{ eV} \sim (10,4)$ $M_{11} \sim 549 \text{ nm}$
- GaAs: $E_g = 1.43 \text{ eV} \sim (6,4)$ $S_{11} \sim 867 \text{ nm}$
- InP: $E_g = 1.35 \text{ eV} \sim (9,1)$ $S_{11} \sim 919 \text{ nm}$

However, there is a fatal drawback in SWCNTs, synthesis of SWCNTs does not produce single pure chirality. CNTs have been produced many synthesis method, arc discharge (ADC) was the first method Sumio Iijima discovered MWCNT in 1991. In order to increase the production efficiency of CNTs, researchers have been developed and improved synthesis methods: laser ablation (LA), chemical vapor deposition (CVD), etc. The CVD is commonly used for CNT growth, cobalt and molybdenum catalysts and CO

gases (CoMoCAT) and high pressure carbon monoxide (HiPCO) techniques are representative to use SWCNT growth among other CVD growth. We purchase SWCNT products from Sigma Aldrich, the product name is SG65i and SG76 which SG means super growth [6], first demonstrated productive method using water assisted CVD method by Kenji Hata [85]. Among synthesis method, SG65i by CoMoCAT is the most selective chirality, approximately 41 % of (6,5) chirality contained [2]. Fig A.3 exhibits diameter variations with several synthesis cases. The diameter of SWCNTs are varied not only the range of diameter but also majority population of diameter depending on the synthesis methods. Although CoMoCAT is the smallest range of diameter variation, this is the reason why sorting process is required for using SWCNTs in order to get specific chirality which we want to apply devices.

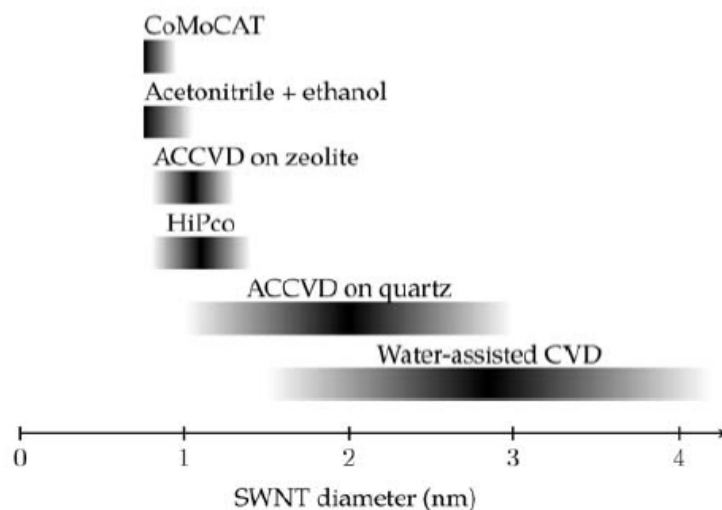


Figure A.3: Large diameter range in each SWCNT synthesis method [56].

A.1.2 Kinds of SWCNT sorting methods

Sorting results have been reported since 2003 starting with ion exchange chromatography methods which acronym is IEX in Fig. A.4. This event is the significant event demonstrating possibility of sorting SWCNTs. Basically SWCNTs are wrapped by DNAs and sorted. Observing this sorting results, there are several sorting methods have been followed. Most of them are using chemical treatment except dielectrophoresis. Dielectrophoresis is an interesting approach that semiconducting and metallic SWCNTs

have different polarizability in external AC signals [124]. This method is one of the conductivity separation methods. According to the separation scope, there are three cases: enantiomers which is direction of SWCNT wrapping right or left, single chirality which is sole chirality, and conductivity [228]. Depending on the methods, separation results are different and we need to select sorting methods related to the purpose of the sorting.

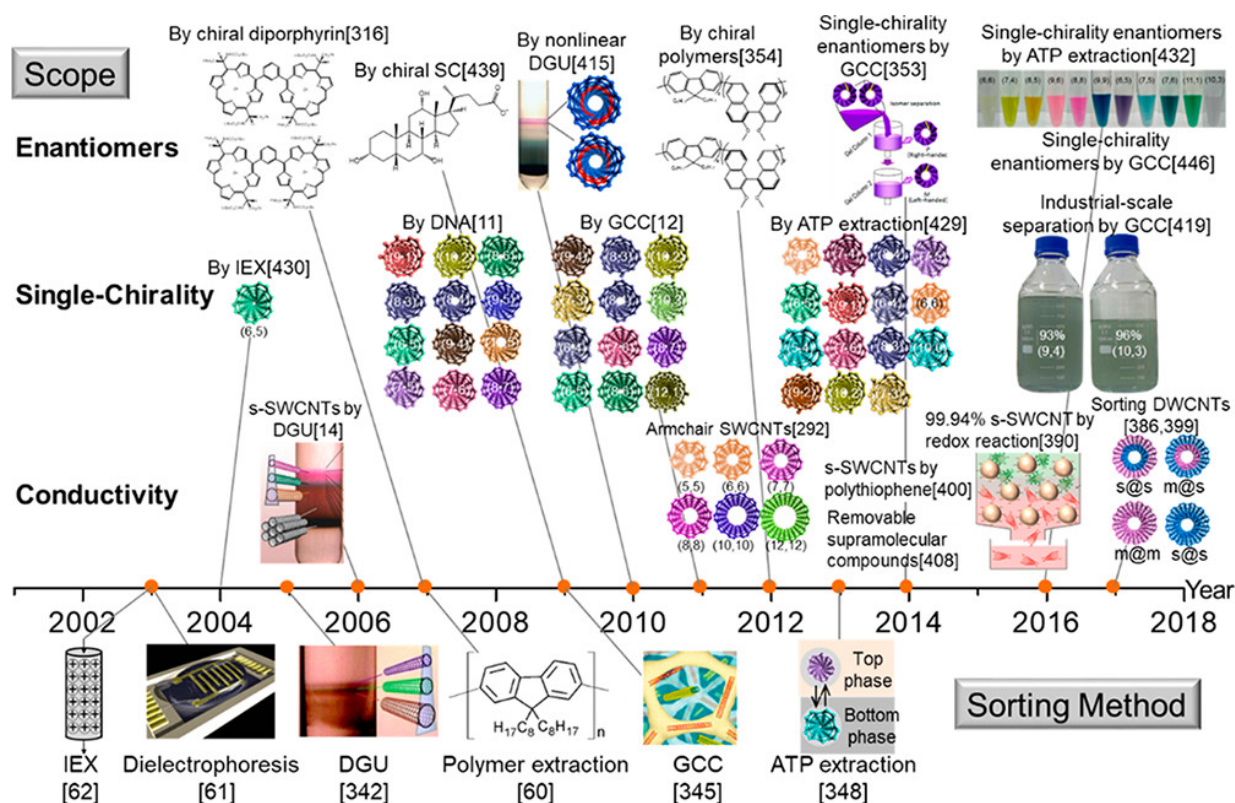


Figure A.4: Lists of SWCNT sorting methods chronologically [228].

The basic concept of SWCNT sorting methods is using external interactions with solution based SWCNTs. Dielectrophoresis is exceptional as it uses electric forces, on the other hand, the majority of sorting methods use additives such as surfactant, biomolecule, aromatic molecule, organic solvent, and polymer in Fig. A.5 [228]. Wrapped or adsorbed SWCNTs are separated by internal or external forces.

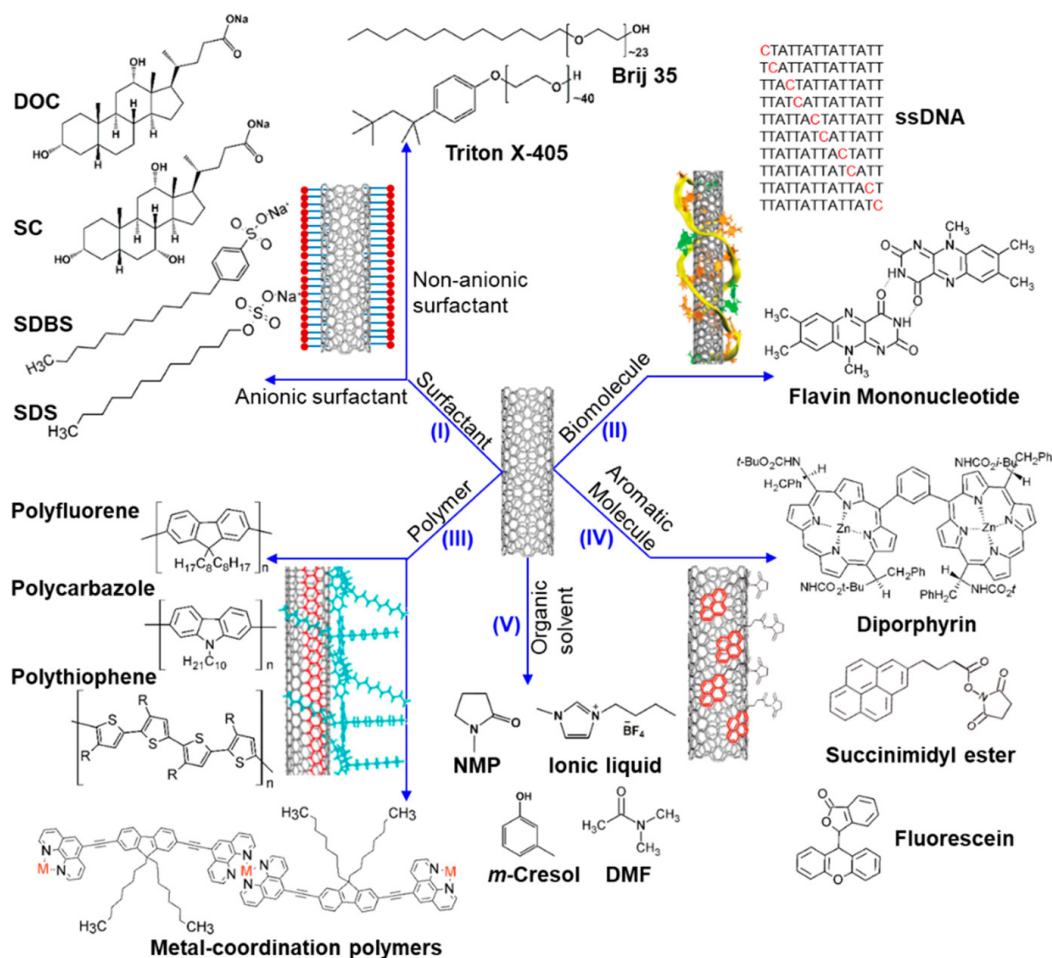


Figure A.5: Case of additives separated by kinds of material groups [228].

A.1.3 Principle of ATPE

ATPE sorting method is relatively young among sorting methods which is developed in 2013. The merits of method are economical, simple and easy process, being able to scale up, and do both metal/semi or diameter separation. Basically, two-phase which is done by two polymers, DX and PEG is required to separate SWCNTs in the solution, DX becomes the bottom phase and PEG becomes the top phase. In order to form the boundary partitioning of two phases, combination of concentration of two polymers is required above biphasic line (Refer to the Appendix D).

Next principle is done by surfactants. There are three surfactants used in ATPE pro-

cess. Depending on the purpose of the separation, DOC and SDS are used for diameter separation or DOC and SC are used for metal/semi separation with NaClO. Surfactants wrap SWCNTs, and hydrophobicity works for determination of where to move SWCNTs, top phase or bottom phase. DX reveals more hydrophilic and PEG more hydrophobic. DOC and SC are hydrophilic and SDS is hydrophobic. Therefore SWCNTs are moving top and bottom phase matching with hydrophobicity. For the diameter separation case, SDS has higher chance to wrap the larger diameter as the molecular form of SDS has a long chain, on the other hand, DOC does not have a long chain. Therefore, SDS tends to wrap the larger diameter moving to the top phase and DOC tends to wrap smaller moving to the bottom phase in diameter separation. For the metal/semi separation, NaClO oxydizes SWCNTs and oxydized SWCNTs are wrapped by SC and moves to the bottom phase. As metallic is easy to be oxydized, metallic SWCNTs goes down to the bottom phase and semiconducting SWCNTs moves to the top phase. Based on the principles, the ATPE process is simplified in Fig. A.6. SWCNTs, polymers, and surfactants are combined and mixed in a vial. This mixture seems mixed but is not well-dispersed solution. The solution becomes separated as time goes by. To reduce the process time, this mixture is centrifuged, our recipe is 1500 g for 3 minutes, and quickly obtained top and bottom sorted results. Take top and do again and again further separation with top and bottom phases.

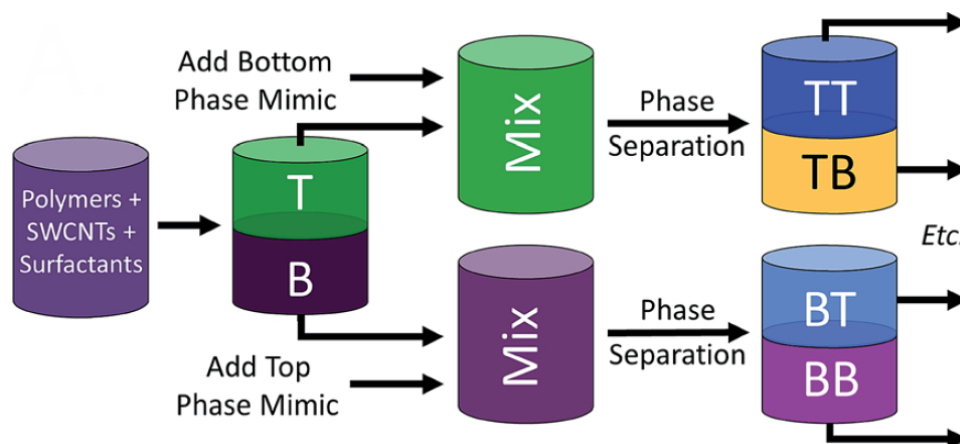


Figure A.6: Scheme of ATPE steps [62].

A.2 Requirements

There are 4 requirements to proceed ATPE: SWCNT solution, polymers & surfactants, pipettes & centrifuge, and UV-vis.

A.2.1 Materials

1. Preparing powder form of SWCNTs

Powder form of SWCNTs are purchased and disperse in water with surfactant.

Product	Distributor	Product number	CNT Type	Synthetic method	Average diameter	Median length
SG65i	Sigma-Aldrich	773735	SWCNT	CoMoCAT	0.78 nm	1 μm
SG76	Sigma-Aldrich	704121	SWCNT	CoMoCAT	0.83 nm	1 μm
SWCNT	Sigma-Aldrich	704113	SWCNT	CoMoCAT	0.7 - 1.3 nm	1 μm
MWCNT	Sigma-Aldrich	698849	SWCNT	CVD	12 nm	10 μm
Purified SWCNT	NanoIntegris		SWCNT	HiPco	0.8 - 1.2 nm	100 - 1 μm

Table A.2: Information of carbon nanotubes which we used for ATPE.

2. Preparing polymer and surfactant stocks and mimics

Preparing stocks and mimics makes ATPE process efficiently.

Mimics are mixture of polymer and surfactants which are commonly used in ATPE Process. It can not only increase efficiency but also reduce concentration uncertainty.

A.2.2 Tools and Equipment

Basically, three main apparatus are need proceeding ATPE steps: vials, pipettes, and centrifuges.

- Vials: Usually used 14.7 mL glass vial. 50 mL tubes are used for larger volume and 4 mL vials keeps small sorted SWCNT solutions.

Product	Maker	Target concentration	Target amount	Solution Polymer or surfactant (volume)	mili-Q water (MQW)	Remark
DX 70k	TCI	20 %(w/w)	45 - 50 mL	10 g (19.5 mL)	40 mL	
PEG 6k	Alfa Aesar	25 %(w/w)	45 - 50 mL	12 g (19.0 mL)	36 mL	
PEG 6k	Alfa Aesar	40 %(w/w)	45 - 50 mL	20 g (32.5 mL)	30 mL	
SDS	Sigma-Aldrich	4.5 %(w/v)	40 mL	1.8 g (4.0 mL)	40 mL	OibXtra > 99 %
DOC	Sigma-Aldrich	4.0 %(w/v)	40 mL	1.6 g (4.0 mL)	40 mL	OibXtra > 98 %
SC	Sigma-Aldrich	4.5 %(w/v)	40 mL	1.8 g (4.0 mL)	40 mL	OibXtra > 99 %
??	Sigma-Aldrich	1/100 th	100 mL	1 mL & 99 mL	10 - 15 % Chlorine	

Table A.3: Table of information of stocks for ATPE. The total volume target is around 45 - 50 mL. (updated 2021.08.16.) [62].

Target Concentration [%]						Original [% , mL]					
DX	PEG	DOC	SDS	SC		DX	PEG	DOC	SDS	SC	MWQ
Dia TM ①	12.5	0.04	0.60			25.0, 7.50	4.0, 0.15	4.5, 2.0		5.35	
Dia TM ②	12.5	0.04	1.20				25.0, 7.50	4.0, 0.15	4.5, 4.0		3.35
Dia BM ①	15.0		0.05			20.0, 11.25		4.0, 0.19			3.56
ms TM ①	12.5			1.2	1.8		40.0, 4.69		4.5, 4.0	4.5, 6.0	

Table A.4: Table of information of mimics for ATPE [62].

- Pipettes: There are automatic pipettes and manual pipettes. Automatic pipettes are used for adding solutions to minimize human errors. Manual pipettes are employed for taking solutions as those are easy to control pressures immediately. (*Refer to "Tips and Troubleshooting" for practical information)
1000 uL pipettes are commonly used for ATPE. So there are two pipettes each kind.

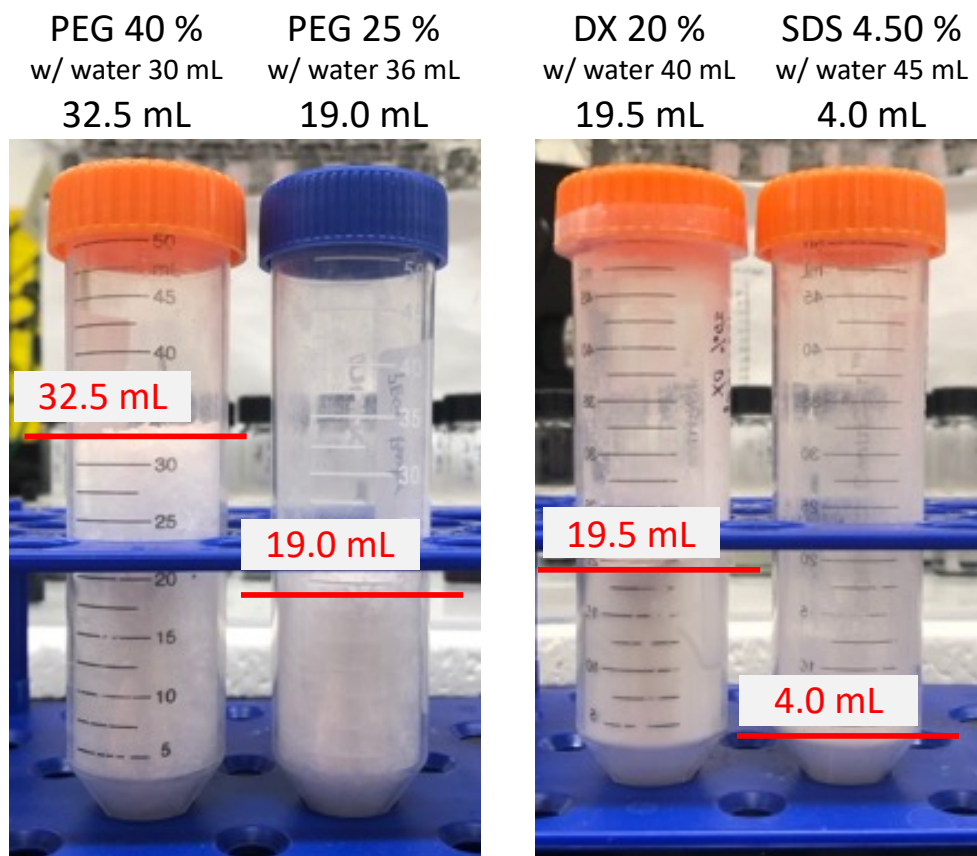


Figure A.7: Photos for the amount of volume of powders: PEG, DX, and SDS.

- Automatic: 3 different volume cases
 - * Range 5 - 100 uL, resolution 0.1 uL (1 ea)
 - * Range 15 - 300 uL, resolution 0.2 uL (1 ea)
 - * Range 50 - 1000 uL, resolution 1.0 uL (2 ea)

- Manual: 5 different volume cases
 - * Range 0.5 - 10 uL, resolution 0.05 uL (1 ea)
 - * Range 10 - 100 uL, resolution 0.1 uL (1 ea)
 - * Range 20 - 200 uL, resolution 1 uL (1 ea)
 - * Range 100 - 1000 uL, resolution 1 uL (2 ea)
 - * Range 500 - 5000 uL, resolution 5 uL (1 ea)

- Sonicator: Two sonicators are mainly operated before doing ATPE to make SWCNT dispersed solutions, bath sonicator and tip sonicator. Bath sonicator also helps dispersing surfactants and polymers in water.
 - Bath sonicator: Taking water in Branson 1510 model upto operation level and Selecting the 'Set Sonics' option for certain times: usually SWCNT dispersions are for 10 minutes, and polymers and surfactants for more than 20 minutes. Using sponges not to fall vials down into the water.
 - Tip sonicator: Q125 by QSONICA, tip sonicator, breaks aggregated SWCNTs after bath sonication as bath sonicator is not enough SWCNT solutions dispersed. There are two tips, the 1/8 inch diameter tip is for 500 μ L - 15 mL and the 1/4 inch diameter tip for 10 mL - 50 mL. The setting condition of tip sonicator operation is 71 % amplitude for 2 seconds on and 1 second off.
- Centrifuge: There are two centrifuges proceed for ATPE: one is ultra-centrifuge doing purification steps which explained in "Process" chapter and the other is centrifuge accelerating two-phase partitioning. Note that Balancing is crucial for the safety and dealing rotors carefully not to be damaged and scratched.
 - Ultra-centrifuge: Optima XE-100 by Beckman Coulter with fixed angle roter Type 70.1 Ti which can contain 12 tubes, 10.4 mL polycarbonate bottles. **Be careful using the ultra-centrifuge.** Balancing is important when adding solutions in the bottles. Please ask Prof. Kim before using this equipment.
 - Centrifuge: ST8 benchtop cntrifuge by ThermoFisher. This centrifuge is for partitioning the mixed solution during ATPE processes accelerating the separation speed. Rotor type is four swing buckets for 50 mL conical tube but 14.7 mL vials are also used in these buckets.
- UV-vis: UV-vis is the one of the easiest way of SWCNT solution base characterization. UV-3100PC model by VWR measures SWCNT solutions by scanning wavelength from 190 nm to 1100 nm to secure the absorbance measuring transmittance. This range covers M_{11} and S_{22} ranges but partially cover S_{22} for CoMoCAT which are SG65i, SG76, and random SWCNTs, and HiPCO. The ranges are summarized in Table A.5.

ATPE process consists of 3 steps: Step1 for dispersion and purification which is preparation steps, Step2 for main ATPE step, and Step3 for characterization and preparation of sorted SWCNTs to future usage.

		CoMoCAT	HiPCO
	Diameter	0.7 - 0.9 nm	0.8 - 1.3 nm
	[Dominant]	[0.7 - 0.8 nm]	[1.1 nm]
Chirality (n,m)		10 < n + m < 13	11 < n + m < 19
UV-vis	S ₁₁	800 nm - 1600 nm	900 nm - 1700 nm
	S ₂₂	500 nm - 800 nm	580 nm - 980 nm
	M ₁₁	400 nm - 580 nm	450 nm - 650 nm

Table A.5: Summary of UV-vis wavelength range of S₁₁, S₂₂, and M₁₁ according to Co-MoCAT and HiPCO.

A.2.3 Step1: Pre ATPE - Dispersion and Purification

SWCNTs are required to be dispersed in water as ATPE is a solution based sorting process. Therefore, dispersion and purification steps are proceeded for preparing SWCNT solutions, which we call 'Parent'.

1. Dispersion

Aim for SWCNT solution is making 1 mg/mL SWCNT concentration solution in 1.0 % DOC.

The 1 mg/mL SWCNT concentration is optimized that more than 2 mg/mL SWCNT is not recommended and DOC 1.0 % is also recommended concentration based on the experimental results although the best efficiency of DOC concentration is 1.6 % [62, 24]. As the precise concentration is essential for this step, scaling the weight of SWCNTs and adding the water amount should be done precisely. Powder form of SWCNTs is taken in the glove box as it is nano particle. The amount of MQW is followed by calculating the weight of SWCNTs and 1 mg/mL concentration. Once the SWCNTs and MQW are coming together in a tube, do bath sonication and tip sonication. Specific steps are as below.

- Weigh a empty 50 mL tube.
- Take SWCNTs in a glove box. (Following the glove box SOP)
- Weigh the total weight of tube and SWCNTs and get the only SWCNT weight.
- Add MWQ, calculating the amount by weight of SWCNT based on the concentration 1 mg/mL.
- Do bath sonication for 10 minutes.
- Do tip sonication for 2 hours with the condition: amplitude 71 %, 2 second on and 1 second off. Use 1/4 inch tip as normally more than 10 mL volume of SWCNT solution is prepared.
(* It takes about 3 hours as 2 hours are only for "On" time.)

2. Purification

Aim for purification step is removing impurities in the solution as it contains catalysts which are residues from SWCNT synthesis, amorphous carbon, and non SWCNT particles by doing ultra-centrifuge.

Two steps of ultra-centrifuge are going for the purification. The first step is relatively lower speed than the second step, 20,000 rpm to remove majority of catalysts and the second step is for removing junks of carbon with 60,000 rpm. Operating ultra-centrifuge is dangerous because the high speed spinning makes enormous force with small amount mass differences. i.e. 20,000 rpm with Type 70.1 Ti rotor generates about 27440 g. The weight differences smaller than 10 mg was okay in our experiment. However, balancing as smaller as possible is recommended for operating the ultra-centrifuge.

Be careful when using ultra-centrifuge. Ask Prof. Kim before use ultra-centrifuge.

- Add and balancing SWCNT solutions in 10.4 mL polycarbonate bottles. If the number of bottles are odd number, prepare a bottle with water.
- Set the bottles in Type 70.1 Ti rotor symmetrically. Refer to the Appendix C.
- Do ultra-centrifuge as the first purification step: 20,000 rpm for 1 hour 45 minutes at 22.
- Take all SWCNT solutions except pellet which is gray color on the bottom wall.

- Preparing the second ultra-centrifuge by balancing with the first purified SWCNT solution.
- Do ultra-centrifuge as the second purification step: 60,000 rpm for 45 minutes at 22.
- Take top 60 % volume of each bottles as top phase naming "2T", next 60 - 95 % as bottom phase naming "2B", and the rests are wastes.
- Cleaning bottles: Only using DI water and q-tips for cleaning the polycarbonate bottles. "DO NOT" use acetone for cleaning.

A.2.4 Step2: ATPE - SG65i - Main Processes

This recipe is set reproduced ATPE sorting results with SG65i at June 21st 2020. This recipe version is focused on reproducibility in terms of steps, colors and amounts referring to Jeffrey Fagan's recipes.

PC step at the beginning is reducing the DOC concentration to make 0.04% during ATPE process as the initial DOC is 1.0 %. This recipe reduces just one step for PC though there are PC two steps in Jeff's recipe. Using mimics can reducing operation time and uncertainty. However, it is not well-equipped in this version.

This is a simplified SG65i separation recipe obtaining semiconducting and metallic SWCNT solutions: Bluegreen color is (7,6) & (7,5) dominant, Purple color is (6,5) dominant, and yellow color is (6,6) dominant. Forestgreen color is extracted at the beginning stage from top phases (T & BT), naming TC solution is combined T & BT, followed by Bluegreen (TCM_t) and yellow (TCM_b) colors are separated metal/semi separation. Bottom phase (2B) looks PurpleBlack color will do metal/semi separation 4 times, then we can secure Purple colors, DarkPurple ($2BM_t$), LittleDarkPurple ($2B2M_bM_t$), Purple ($2B3M_bM_t$) and LightPurple($2B4M_bM_t$), which are (6,5) & (6,4) dominant SWCNT solutions. $2B5M_b$ is Yellow but it is (7,4) & (5,5) dominant.

*** If the color of BT and $2B3M_bM_t$ are not clear, those are BlueGreen or Purple, do more ATPE steps following 2B step or $2B3M_b$ of same condition.**

- The mixing order is following the list order in "Mixing" solutions
- Stage1: Parent $\rightarrow$ PC
 - * Mixing - (Parent 2 mL) + (MQW 3 mL) + (20 % DX 3 mL) + (25 % PEG 4 mL)
 - * Results - (Top: LightGray 9.5 mL $\rightarrow$ Discard)

- (Bottom: PC - Black 2.5 mL → Diameter separation)

- Stage2: PC → T & B
 - * Mixing - (PC 2.5 mL) + (MQW 1 mL) + (20 % DX 2 mL) + (25 % PEG 3 mL) + (4.5 % SDS 1.6 mL)
 - DOC 0.041 %, SDS 0.71 %
 - * Results - (Top: T - DarkForestGreen 6 mL → Combined with BT)
 - (Bottom: B - Black 4 mL → Diameter separation)

- Stage3: B → BT & 2B
 - * Mixing - (B 2.5 mL) + (Dia TM ① 2 mL) + (Dia TM ② 1 mL)
 - DOC 0.041 %, SDS 0.75 %
 - * Results - (Top: BT - LightForestGreen 3 mL → Combined with T)
 - (Bottom: 2B - PurpleBlack 4 mL → Metal/semi separation)

- Stage4: Combining T & BT → Collapsing, TC
 - * Mixing - (T 6 mL) + (BT 3 mL) + (20 % DX 2 mL) + (25 % PEG 1 mL) + (4.0 % DOC 0.15 mL) + (1.0 % DOC 0.15 mL)
 - ζ DOC 0.09 %
 - * Results - (Top: Clear 10.3 mL → Discard)
 - (Bottom: TC - DarkForestGreen 2 mL → Metal/semi separation)

- Stage5: TC → TCM_t & TCM_b
 - * Mixing - (TC 2 mL) + (20 % DX 1.5 mL) + (25 % PEG 2.5 mL) + (4.5 % SC 1.8 mL) + (4.5 % SDS 1.16 mL) + (1/100 NaClO 71.7 μL) + (Wait about 3 minutes)
 - SC 0.9 %, SDS 0.7 %
 - * Results - (Top: TCM_t - DarkBlueGreen 5.5 mL → Keeping)
 - (Bottom: TCM_b - Yellow 3 mL → Keeping)

- Stage6: 2B → 2BM_t & 2BM_b
 - * Mixing - (2B 4 mL) + (25 % PEG 3.5 mL) + (4.5 % SC 2.4 mL) + (4.5 % SDS 2.3 mL) + (1/100 NaClO 97.6 μL) + (Wait about 3 minutes)
 - SC 0.88 %, SDS 1.09 %
 - * Results - (Top: 2BM_t - DarkPurple 8 mL → Keeping)

- (Bottom: $2BM_b$ - PurpleBlack 4 mL $\rightarrow$ Metal/semi separation)

- Stage7: $2BM_b \rightarrow 2BM_bM_t$ & $2B2M_b$
 - * Mixing - ($2BM_b$ 4 mL) + (20 % DX 0.5 mL) + (25 % PEG 2 mL) + (4.5 % SC 0.92 mL) + (4.5 % SDS 1.12 mL) + (1/100 NaClO 68.3 μ L) + (Wait about 3 minutes)
 - SC 0.89 %, SDS 1.09 %
 - * Results - (Top: $2BM_bM_t$ - LittleDarkPurple 4 mL $\rightarrow$ Keeping)
 - (Bottom: $2B2M_b$ - DarkYellow 4 mL $\rightarrow$ Metal/semi separation)
- Stage8: $2B2M_b \rightarrow 2B2M_bM_t$ & $2B3M_b$
 - * Mixing - ($2B2M_b$ 4 mL) + (20 % DX 0.5 mL) + (25 % PEG 2 mL) + (4.5 % SC 0.92 mL) + (4.5 % SDS 1.12 mL) + (1/100 NaClO 68.3 μ L) + (Wait about 3 minutes)
 - SC 0.89 %, SDS 1.09 %
 - * Results - (Top: $2B2M_bM_t$ - Purple 4 mL $\rightarrow$ Keeping)
 - (Bottom: $2B3M_b$ - PurpleYellow 4 mL $\rightarrow$ Metal/semi separation)
- Stage9: $2B3M_b \rightarrow 2B3M_bM_t$ & $2B4M_b$
 - * Mixing - ($2B3M_b$ 4 mL) + (20 % DX 0.5 mL) + (25 % PEG 2 mL) + (4.5 % SC 0.92 mL) + (4.5 % SDS 1.12 mL) + (1/100 NaClO 68.3 μ L) + (Wait about 3 minutes)
 - SC 0.89 %, SDS 1.09 %
 - * Results - (Top: $2B3M_bM_t$ - LightPurple 4 mL $\rightarrow$ Keeping)
 - (Bottom: $2B4M_b$ - Yellow 4 mL $\rightarrow$ Keeping)
- Final Solutions (Ver. 2020. 06. 22.)
 - TCM_t - DarkBlueGreen, 5.5 mL (Semi $\sim$ 97 - 98 %, (7,6) & (7,5) $\sim$ 68 %)
 - TCM_b - Yellow, 3 mL (Metallic $\sim$ 70 %)
 - $2BM_t$ - DarkPurple, 8 mL (Semi $\sim$ 81 %, (6,5) & (6,4) $\sim$ 67 %)
 - $2BM_bM_t$ - LittleDarkPurple, 4 mL
 - $2B2M_bM_t$ - Purple, 4 mL
 - $2B3M_bM_t$ - LightPurple, 4 mL
 - $2B4M_b$ - Yellow, 4 mL (Metallic $\sim$ 50 %)

A.2.5 Step3: Post ATPE - UV-vis, Polymer exchange, and Centrifuge

Post ATPE step is characterization of sorted SWCNT solutions measuring absorbance by UV-vis, removing polymers by polymer exchange steps, and removing impurities by centrifuge.

1. Characterization by UV-vis

Two-step processes can obtain chirality and purity: Measure absorbance by UV-vis equipment, UV-3100PC by VWR and fit, subtract, and calculate chirality and purity by UV-vis GUI.

(a) UV-vis

- Turn on UV-3100PC and computer: wait about 15 minutes.
(Use the lamp U2 and W)
- Calibrate with DI-water 3 times.
(Fill DI-water in a cuvette and set in UV-3100PC "100" label on the cuvette left side)
(Click "Z" button and waiting calibration, and measure absorbance)
(Iterate twice)
- Add SWCNT solutions in the cuvette and measure it.
(Some solutions are so dark that those are not measured well, peaks are not clearly captured. Diluting dark solutions by adding DI-water)
(Parent: SWCNT solution 25 μL + DI-water 200 μL)
(TCM_t - DarkBlueGreen 50 μL + DI-water 100 μL)
(2BM_t - DarkPurple 50 μL + DI-water 150 μL)
(2BM_bM_t - LittlePurple 50 μL + DI-water 125 μL)
(2B2M_bM_t - Purple 100 μL + DI-water 100 μL)
(Others: original solutions 150 μL)
- Save measurement results .sca and .csv format.
(.sca: UV-3100PC software format)
(.csv: to analyze in laptop using extract function)
- Cleaning cuvette.
(Using DI-water and blowing N₂)
(Do not touch the beam path window. If it is dirty, wiping with ethanol)

(b) Fitting absorbance results

- Open "main.py" in ATPE_Data_Analysis_V2_5

- Open csv files of results and set store folder
- Do "Model Background" varied start and end ranges
(Initial range is 440 - 880 nm. Change the range observing the plot)
- Do "Analysis Spectrum" with the best model fit range
(Results are automatically displayed and stored csv format.)

2. Polymer exchange

Polymers and high concentration of surfactants assisting ATPE processes are not preferable for SWCNT usages like SWCNT film for electronic or optical devices. Two ways of polymer exchange remove polymers and reduce surfactant concentration.

- Polymer exchange by centrifuge
It take long time with small volume of SWCNT solutions.
 - Add sorted SWCNT solution 2 mL in Amicon Ultra-15 and fill the rest volume about 10 mL with 0.04 % DOC.
 - Centrifuge set 4500 rpm for 30 minutes.
(DX based solution takes longer centrifuge time, sometimes it takes longer than 2 hours.)
(Centrifuge until 200 μ L left on the bottom)
 - Iterate 4 more times.
- Polymer exchange by Amicon Stirred Cell
Large volume is good to be proceeded this method. Be careful controlling pressure as high pressure damage membrane: $\leq$ 10 psi recommended.
 - Connect pressure pump and set membrane in Amicon Stirred Cell.
 - Add sorted SWCNT solution 5 mL in Amicon Stirred Cell and fill the rest volume about 45 mL with 0.04 % DOC.
 - Turn on the pressure pump and wait filtration until 5 mL left.
(Normally, it takes about 7 - 10 minutes.)
 - Iterate twice more.
- Collecting exchanged solutions with filtered SWCNTs which are on the membrane filter in vial or tube, do tip sonication to make well-dispersed SWCNT solutions.
(Depending on the amount, use 1/8 inch or 1/4 inch tip.)
(Set condition: 71 % amplitude, 2 seconds on and 1 second off for 1 hour)

3. Centrifuge to remove impurities Sorted SWCNT solutions can be a high chance to be contaminated during ATPE, characterization, polymer exchange, and sonication. Therefore, centrifuge step is required to remove impurities. (Normally, the amount is small, total amount $\leq$ 14 mL, ST8 centrifuge is used.)
- Add sorted SWCNT solutions in microtubes and balance them.
 - Set 10,000 rpm for 1 hour and centrifuge.

A.3 Tips and Troubleshooting

A.3.1 Pipetting

- Automatic pipettes for adding solutions, manual pipettes for extracting solutions. (Reason: Addition parts are required precise amount minimizing human errors. Whereas, extraction parts are needed varied pressure controls from time to time separating surface of boundaries.)
- DX is so viscous that dispensing and extracting speeds should be slow. Normally, extracting 4 and dispensing 2 in automatic setting. PEG 40 % also needs same condition.
- Extraction protocol: Doing at least one more extracting attempt as solutions does not come from pipette tips. For DX or high viscous solutions, waiting several seconds and repeat two or more times. This is crucial for reproducible results.
- When extract SWCNT sorted solutions, sometimes two phase solutions are mixed by pipetting. Then, do centrifuge again in order to make clean boundary and extract again.
- Two tips for extraction: The first tip is holding parts, using two fingers for pushing and pulling the knob and the second tip is holding tips sustaining the height of solution, especially when the tip is near a boundary. (This tips are not easy to explain through paper. Please refer to the video which is done by Jeffrey Fagan.)

A.3.2 Surfactant

- Do not exceed 1.2 % SDS concentration
(Reason: SWTNs become bundled in such a high concentration of SDS.)

A.3.3 Polymer

- Degradation of PEG: Do not verified the duration after becoming a PEG solution. However, long storage period of PEG does not work on separation of PEG.
(Reason: There were observations with long storage period PEG which the PEG affects DOC concentration become lower by taking out DOC from the solution. And certain concentration of mixed PEG and DOC form a pudding like phase instead of solution.)
- Bacteria in DX: Barteria is created in long storage period of DX, more than several days.
(Currently do not specified exact date, but it is not recommended storing more than 3 days in room temperature.) And always keep in a fridge after ATPE. Bacteria does not eat DOC, but it may affect ATPE quality. Bacteria in solution can be removed by centrifuge, bacteria looks like white particles at the bottom of the microtube.
(The condition of centrifuge is 10,000 rpm for 1 hour with ST8, 75005715 rotor. This condition is not verified for optimization.)
Bacteria is observed in example samples on the shelf.

A.3.4 Two-phase diagram in polymers

- Without two-phase in polymers, ATPE does not work. Make sure the concentration of two polymers is above biphasic line in phase diagram. If two polymers are in the biphasic region, mixture becomes murky. If it is not, the mixture looks clear.

A.4 Table of Chirality matched information [223, 77]

Chirality	d_t (nm)	E_{11}	λ_{11}	E_{22}	λ_{22}	λ_{11} UV-vis	λ_{22} UV-vis	Remark
(6,4)	0.692	1.420	873	2.146	578	888	583	GaAs 1.43 eV
(7,3)	0.706	1.250	992	2.457	505	1,005	507	
(6,5)	0.757	1.270	976	2.190	566	986	570	Green2
(9,1)	0.757	1.359	912	1.794	691	924	695	InP 1.35 eV
(8,3)	0.782	1.303	952	1.863	665	962	667	
(10,0)	0.794	1.073	1,156	2.307	537	1,175	539	Green1
(9,2)	0.806	1.090	1,138	2.251	551	1,150	555	
(7,5)	0.829	1.211	1,024	1.921	645			
(8,4)	0.840	1.116	1,111	2.105	589	1,125	591	
(10,2)	0.884	1.177	1,053	1.683	737	1,065	739	
(7,6)	0.895	1.107	1,120	1.914	648	1,135	650	Red2
(9,4)	0.916	1.126	1,101	1.716	722	1,117	726	
(10,3)	0.936	0.993	1,249	1.963	632	1,272	638	Red1
(8,6)	0.966	1.057	1,173	1.727	718	1,187	720	
(9,5)	0.976	0.999	1,241	1.845	672	1,267	674	
(7,4)	0.766	2.650	468					Blue
(6,6)	0.825	2.710	458					
(9,3)	0.859	2.430	511					
(8,5)	0.902	2.480	500					
(7,7)	0.963	2.480	500					GaP 2.26 eV
(10,4)	0.992	2.220	559					

Table A.6: Table of SWCNT transition energy and wavelength. Updated table in thesis appendix [228].

A.5 Color of sorted SWCNTs

Exmamples of sorted SWCNT solution colors.

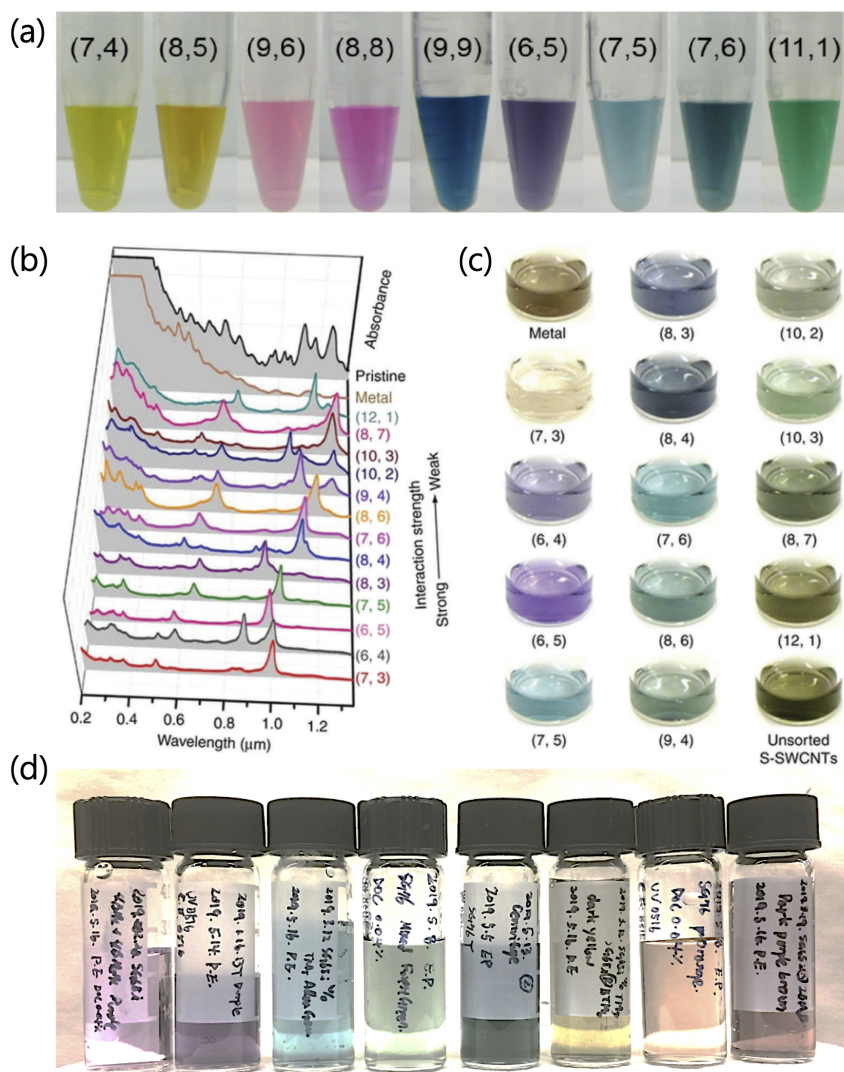


Figure A.8: (a) SWCNT solution colors separated by DNA engaged method [235]. (b) and (c) are Spectrum and colors of sorted SWCNTs by gel chromatography [104]. (d) Sorted SWCNTs by ATPE in our lab.

A.6 A Guide to Balanced Centrifuge Loads

Making balance in a rotor is crucial steps for the safe operation of centrifuge. Symmetry is the basic principle.

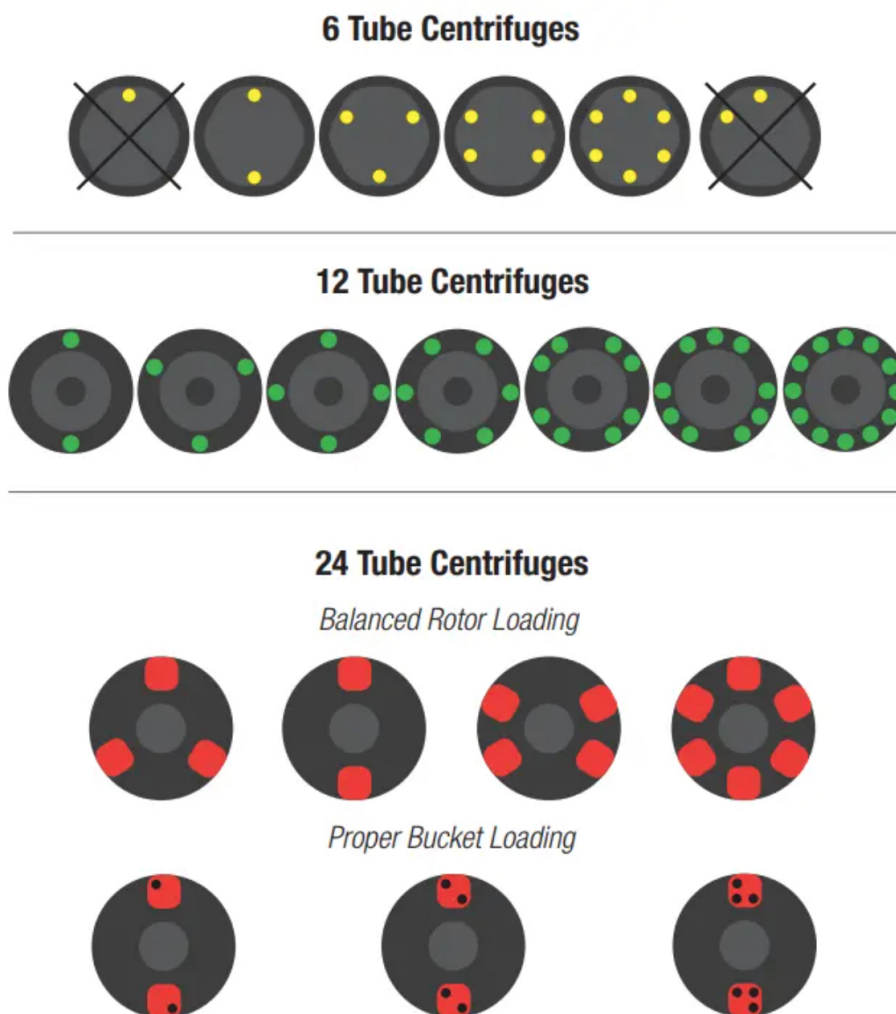


Figure A.9: Examples of loading samples in a rotor to make balance [1].

A.7 Two-phase Diagram: Mixture of DX & PEG

Two-phase states are required the concentration which is above biphasic line. Green is DX and PEG only case and red is DX and PEG with surfactant case which Jeffrey Fagan was done. Adding surfactant case needs higher concentration of polymer mixture to make the biphasic line. Red circle with white dots are experimental results in our lab, it is almost overlapped on Jeffrey Fagan's result.

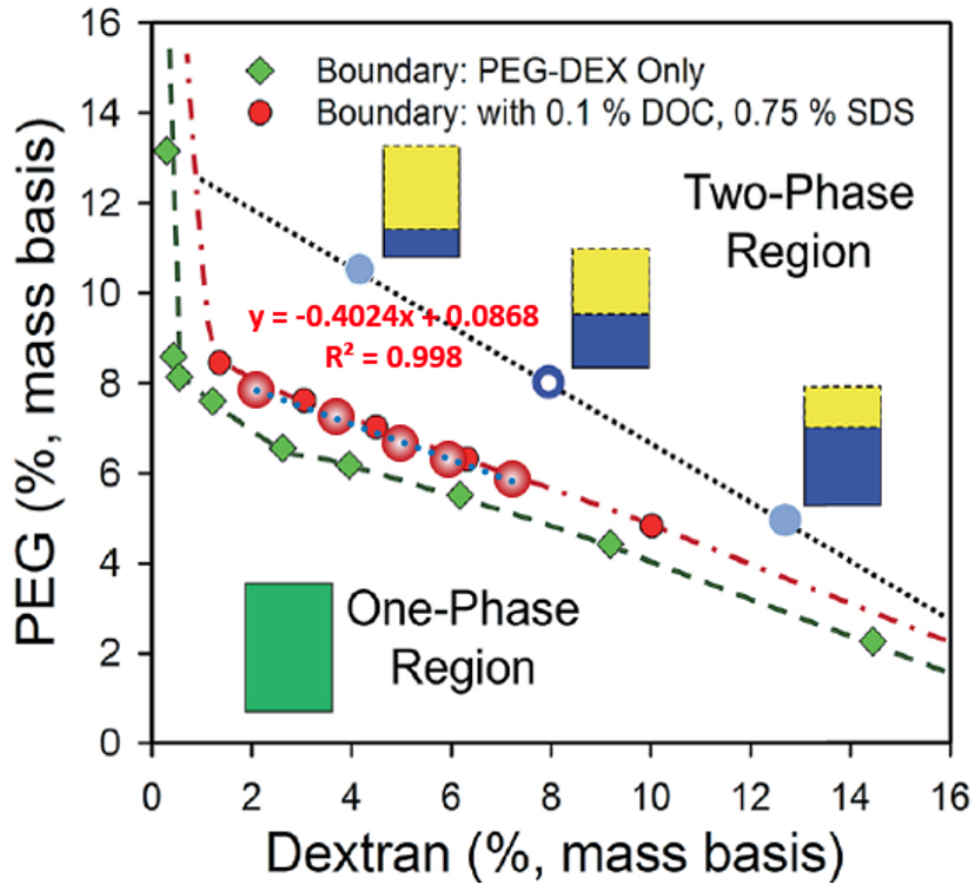


Figure A.10: Phase diagram for DX and PEG. Green is only DX and PEG case, red is DX and PEG with surfactant [62]. Red circle symbol with white center is test results in our lab which is almost overlapped on Jeffrey Fagan's results.