RESEARCH AND DEVELOPMENT OF ORGANIC UV-Vis-NIR PHOTODETECTOR

M.Tech Thesis

By

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DISCIPLINE OF ELECTRICAL ENGINEERING

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RESEARCH AND DEVELOPMENT OF ORGANIC UV-Vis-NIR PHOTODETECTOR

A THESIS

Submitted in partial fulfillment of the
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RUSHIKESH HAKE

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **RESEARCH AND DEVELOPMENT OF ORGANIC UV-Vis-NIR PHOTODETECTOR** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF TECHNOLOGY** and submitted in the **DISCIPLINE OF ELECTRICAL ENGINEERING, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from June, 2022 to June, 2023 under the supervision of Professor Vipul Singh, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

05-06-2023

Signature of the student with date

(RUSHIKESH HAKE)

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

05/06/2023

Signature of Thesis Supervisor #1 with date

(Prof. VIPUL SINGH)

RUSHIKESH HAKE has successfully given his **M.Tech.** Oral Examination held on **11/05/2023**.

05/06/2023

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Signature of PSPC Member #1
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Signature of PSPC Member #2
Date:

Signature of Head of Discipline
Date:

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Dated: **(Rushikesh Hake)**

Dedicated to My Thesis Supervisor

(Prof. Vipul Singh)

ABSTRACT

In recent years, there has been a significant increase in the demand for consumer electronic products. According to a report by ID Tech Ex, it is projected that the market share of these devices will reach a substantial value of \$330.3 billion by 2027.

To meet the growing demand, organic and hybrid organic/inorganic photodetectors have emerged as promising alternatives to traditional inorganic photodetectors. These photodetectors offer the potential for cost-effective and low-temperature solution-based processing on flexible substrates, enabling large-scale production through roll-to-roll fabrication. However, the performance of these organic/hybrid photodetectors has been somewhat unsatisfactory, limiting their applications. To enhance their performance, it is crucial to have a comprehensive understanding of how to optimize both material composition and processing parameters. The main objective of this dissertation is to improve the performance of hybrid photodetectors by enhancing material properties and designing innovative device architectures. Specifically, the focus is on developing hybrid photodetectors based on ZnO/P3HT-small molecule blend materials for healthcare applications in the near-infrared (NIR) range.

Organic electronics have become commercially viable technology with applications in various fields, including organic solar cells (OSCs), organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photodiodes (OPDs).

Photodetectors play a critical role in diverse industries such as military, medical science, scientific research, space exploration, traffic management, and consumer electronics.

In various organic optoelectronic devices, the active layers typically consist of π-conjugated organic semiconductor materials, which can be polymers or organic small molecules. Small molecule-based devices have shown superior performance in

terms of high carrier mobility, improved ambient stability, and a wide range of tunability in optical and electrical properties compared to polymer-based devices. However, the fabrication techniques for small molecule-based devices are often costly.

To address the cost-effectiveness challenge and enable the fabrication of solution-processed devices, one approach is to blend or mix small molecule materials with highly soluble materials such as polymers.

The primary goal of this work is to fabricate hybrid NIR photodetectors by blending the conjugated polymer (CP) P3HT and the small molecule (SM) Squarine Dye. The impact of blending CP and SM on photodetector parameters and device performance metrics is investigated. The dissertation is divided into three parts:

Study of the chemical structure and properties of the inorganic semiconductor material ZnO, as well as the organic semiconducting material conjugated polymer P3HT and the small molecule Squarine Dye, to facilitate the fabrication of NIR hybrid organic photodetectors.

Fabrication of ZnO/P3HT UV-Vis hybrid photodetectors: This involves creating a dual-wavelength tuned photodetector capable of detecting near-ultraviolet (UV) light at 370 nm and visible light at 520 nm using ZnO and P3HT. The resulting photodetector exhibits a photo sensitivity of approximately 584 and 54 at 370nm and 520nm respectively.

Fabrication of ZnO/P3HT:Squarine Dye NIR hybrid photodetectors: The objective here is to enhance the performance of the photodetector in the NIR region by employing simple, cost-effective, solution processing techniques to blend CP with SM. The resulting hybrid photodetector is based on a ZnO/P3HT:Squarine Dye blend, aiming to achieve a rectification ratio of approximately 218 .

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LIST OF NOMENCLATURE & ACRONYMS

NOMENCLATURE

α	Absorption coefficient
λ	Wavelength [nm]
A	Absorbance
c	Speed of light in vacuum
e	Electronic charge
E_g	Bandgap energy
E_{ph}	Photon energy
h	Planck's constant
I	Incident light intensity
I_d	Dark current
I_{ph}	Photo current

ACRONYMS

D^*	Specific detectivity
DI	De-ionised

EDX	Energy dispersive X-ray
EQE	External quantum efficiency
FESEM	Field emisson scanning electron microscopy
HMTA	Hexamethylenetetramine
IPA	Iso-propyl alcohol
NIR	Near-infrared
PD	Photodetector
PL	Photoluminescence
PVD	physical vapor deposition
R	Photoresponsivity
S	Photosensitivity
UV	Ultraviolet
Vis	Visible light
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
P3HT	Poly(3-hexylthiophene-2,5-diyl)

Chapter 1

Introduction

Electronic devices have had a profound impact on our lives, transforming various aspects of society. Photodetectors, in particular, have emerged as versatile tools with widespread use in commerce, industry, entertainment, research, and various technological applications.

The demand for integrated optical sensors that are large-area, user-friendly, and cost-effective has led to the exploration of novel applications like wearable electronics and implantable biomedical devices. Traditional rigid technologies face challenges in meeting these requirements, prompting increased interest in organic semiconductors as an alternative.[1][2]

Current research efforts are focused on developing organic-inorganic hybrid devices that combine the strengths of both types of semiconducting materials. This work specifically focuses on a hybrid photodetector that combines zinc oxide (ZnO) and poly(3-hexylthiophene) (P3HT), as well as a blend of P3HT and Squaraine dye. By leveraging the unique properties of inorganic and organic semiconductors, this hybrid photodetector aims to achieve improved performance and functionality.[3][4]

To understand the principles underlying these devices, it is essential to explore the fundamentals of inorganic and organic semiconductors. This chapter provides an overview of the key concepts and principles relevant to ZnO-P3HT based hybrid photodetectors. By investigating the synergistic interplay between these two semiconductor types, researchers aim to unlock new possibilities and advancements in the field[5][6][7].

1.1 Photodetector: A Brief Description

A photodetector is an electronic device that detects and measures light or electromagnetic radiation by converting photons

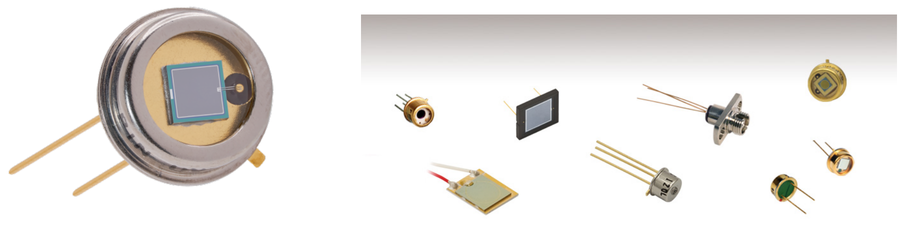


Fig. 1.1: **Some Commercially Available Photodetectors[12][13]**

into an electrical signal. It finds applications in telecommunications, imaging systems, environmental monitoring, medical diagnostics, and scientific research.

Photodetectors operate based on the photoelectric effect, where photons transfer energy to semiconductors, creating a photocurrent that is amplified for analysis. Different types of photodetectors, such as photodiodes, phototransistors, and CCDs, offer various advantages and limitations suited for different applications.

Advancements in photodetector technology have resulted in highly sensitive and compact devices. Integration with other electronic components has enabled integrated optical systems with enhanced functionality[8][9].

Ongoing research focuses on novel materials like organic semiconductors and perovskites, as well as innovative device structures, to improve efficiency, widen the spectral range, and increase flexibility.

Photodetectors have a significant impact on fields like telecommunications, healthcare, research, and consumer electronics, driving advancements in optical sensing and communication systems. They contribute to innovations in optics and photonics, opening new possibilities across various industries[10][11].

1.1.1 Application of Photodetectors

Photodetectors find widespread applications across various fields, including military, medical science, scientific research, space technology, traffic control, consumer electronics, and more[3][8]. Some of the common applications of photodetectors include:

1. Color sensor element for digital cameras

2. Automatic traffic lighting controls
3. Fiber-optic communication systems
4. Optical scanners
5. Photography
6. Security screening
7. Machine vision
8. Wireless LAN (Local Area Network)
9. Remote control devices
10. Industrial automation

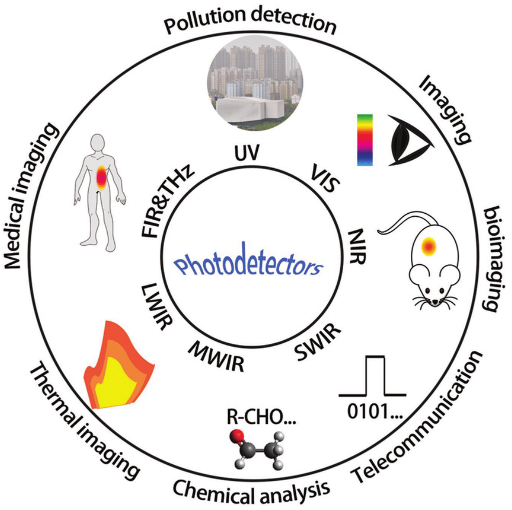


Fig. 1.2: **Applications of photodetector[14]**

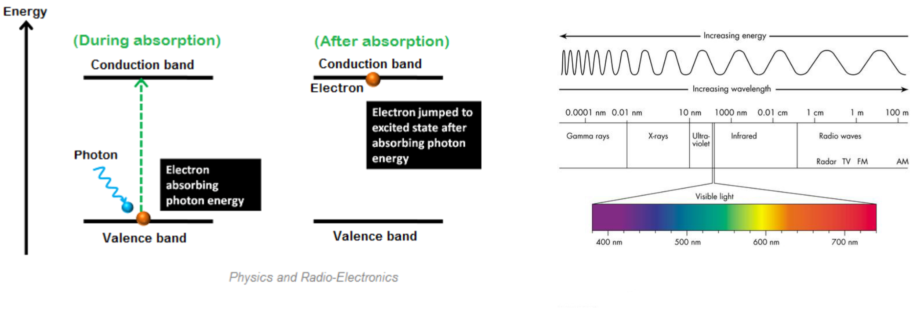
In scientific research, photodetectors are extensively used in applications such as particle detectors and photomultipliers for detecting photons. Image sensors, such as digital charge-coupled devices (CCD) and complementary metal-oxide-semiconductor (CMOS) active pixel sensors, rely on photodetectors for capturing images[15][8].

There are also specific types of photodetectors that convert light energy into other forms of energy. For example, bolometers measure electromagnetic radiation by heating the material, while radiometers sense light pressure to measure electromagnetic radiation.

Figure 1.2 illustrates some examples of commercial applications where photodetectors are utilized.

1.1.2 Working Principles of Semiconductors based Photodetectors

The fundamental principle underlying the process of photo detection is the internal photoelectric effect. When light interacts with the surface of a semiconductor material, and if the energy of the incident photons $E_{ph} = \frac{hc}{\lambda}$ exceeds the energy bandgap of the material E_g, it is absorbed. This absorption leads to the generation of an electron-hole pair, where an electron is excited from the valence band to the conduction band, leaving behind a hole in the valence band,Figure 1.3 [10][6].



((a)) *((b))*

Fig. 1.3: **Schematic of (a) Photoelectric Effect[16] (b) Spectrum of Light[17]**

These generated electron-hole pairs then separate and move towards their respective electrodes under the influence of an intrinsic or externally-applied electric field. This movement of carriers results in the generation of photocurrent in the external circuit. The magnitude of the photocurrent is directly proportional to the intensity of the incident light [1][2]

1.1.3 Classification of Photodetectors

Photodetectors are devices that convert light signals into electrical signals. They play a crucial role in various applications, including imaging, sensing, communication, and optical data storage. Photodetectors can be classified into several major categories based on their operating principles and the materials used. Below are concise explanations of several key classifications of photodetectors, which are determined by the semiconductor material utilized in their construction[18][19]. These types include:

1. **Inorganic Photodetector:** Inorganic photodetectors, also known as semiconductor photodetectors, employ inorganic materials such as silicon (Si), gallium arsenide (GaAs), or indium gallium arsenide (InGaAs) to detect and convert light into an electrical signal. These materials offer high sensitivity, low noise, and fast response times. Inorganic photodetectors are widely used in various applications, including telecommunications, imaging, astronomy, and scientific research [**14**].

2. **Organic Photodetector:** Organic photodetectors (OPDs) are devices that utilize organic semiconductors to detect and convert light into an electrical signal. These semiconducting materials are typically carbon-based polymers or small molecules. OPDs offer advantages such as flexibility, lightweight, and low-cost manufacturing. They find applications in areas such as optoelectronics, imaging sensors, and solar cells[20].

3. **Hybrid Organic-Inorganic Photodetector:** Hybrid organic-inorganic photodetectors combine the advantages of both organic and inorganic materials. These devices utilize a combination of organic semiconductors and inorganic materials, such as metal oxides or perovskites, to achieve enhanced performance. The organic component provides flexibility and large-area coverage, while the inorganic component offers improved charge transport and stability. Hybrid photodetectors exhibit high sensitivity, tunability, and compatibility with different light wavelengths, making them suitable for a range of applications, including photovoltaics, sensing, and imaging[21].

These are some of the major classifications of photodetectors.Each type has its own advantages and is suitable for specific applications based on factors such as sensitivity, speed, spectral range, and cost. Ongoing research and development in this field continue to improve the performance and expand the capabilities of photodetectors.

1.2 Inorganic Semiconductors

Inorganic semiconductors are widely used materials with electrical conductivities between metals and insulators. They are composed of elements from the periodic table and have a crystalline structure. Doping modifies their conductivity by introducing impurities. Inorganic semiconductors offer high electron mobility, thermal stability, and excellent optical properties. They are used in transistors, diodes, solar cells, LEDs, and more. Ongoing research aims to improve their efficiency, stability, and cost-effectiveness, driving advancements in thin-film solar cells, flexible electronics, and optoelectronics. Inorganic semiconductors are crucial for modern technology and the semiconductor field[22][23].

1.2.1 Charge Transport in Inorganic Semiconductors

Charge transport in inorganic semiconductors refers to the movement of electric charge, typically electrons or holes, through the material. It plays a critical role in the functionality of electronic devices and determines their performance characteristics[18][22][24]. Here is a brief description of charge transport in inorganic semiconductors:

1. **Electron and Hole Mobility:** In inorganic semiconductors, charge transport occurs through the movement of electrons and holes. Electrons carry negative charge and move in response to an electric field, while holes represent the absence of an electron and behave like positively charged particles. The mobility of electrons and holes refers to their ability to move through the crystal lattice when subjected to an electric field.

2. **Band Structure:** Inorganic semiconductors have a characteristic energy band structure that influences charge transport. The valence band contains electrons tightly bound to atoms, while the conduction band holds electrons that can move more freely. The energy gap between these two bands, known as the bandgap, determines whether a semiconductor is an insulator or a semiconductor. In semiconductors, the bandgap is small enough for thermal excitation to promote electrons from the valence band to the conduction band, allowing for charge transport.

3. **Impurities and Doping:** The conductivity of inorganic semiconductors can be modified by introducing impurities,

a process called doping. Doping introduces atoms of other elements into the crystal lattice, either to increase the number of free charge carriers (n-type doping) or to decrease their number (p-type doping). This alteration of the material's composition and charge carrier concentration significantly impacts charge transport.

4. **Drift and Diffusion:** Two mechanisms contribute to charge transport in inorganic semiconductors: drift and diffusion. Drift refers to the movement of charge carriers in response to an electric field. When an electric field is applied, electrons and holes experience a force and move towards the opposite electrode. Diffusion, on the other hand, involves the random movement of charge carriers due to thermal energy. This random motion leads to the gradual spreading of charge carriers throughout the material.

Understanding and optimizing charge transport in inorganic semiconductors is crucial for designing efficient electronic devices. Factors such as material composition, crystal structure, doping levels, and applied electric fields all influence the mobility and behavior of charge carriers, impacting device performance and overall functionality.

1.2.2 Types of Inorganic Photodetectors

Inorganic semiconductor photodetectors are devices that convert light signals into electrical signals. They are widely used in various applications, including imaging, sensing, and communication. Here is a brief description of some common types of inorganic semiconductor photodetectors:

1. **Photodiodes:** Photodiodes are one of the most common types of photodetectors. They are based on a p-n junction structure in which the incident light generates electron-hole pairs. The generated carriers are then separated and collected, resulting in a photocurrent. Photodiodes offer high sensitivity, fast response times, and low noise, making them suitable for a wide range of applications.

2. **Photoconductor:** Photoconductor-based photodetectors utilize the change in electrical conductivity of inorganic semiconductors when exposed to light. These devices typically consist of a bulk or thin-film layer of photoconductive

material, such as amorphous silicon (a-Si) or cadmium sulfide (CdS). Incident light generates electron-hole pairs, increasing the conductivity of the material and resulting in a change in current or voltage. Photoconductor-based photodetectors are suitable for a wide range of applications and offer good sensitivity to various wavelengths.

3. **Phototransistors:** Phototransistors are similar to photodiodes but with the addition of a transistor amplification stage. They consist of a light-sensitive base region and two additional terminals: the collector and emitter. Incident light generates carriers in the base region, modulating the transistor's current flow. Phototransistors offer higher gain and amplification capabilities compared to photodiodes, making them suitable for applications where higher sensitivity is required.

4. **Avalanche Photodiodes (APDs):** Avalanche photodiodes are specialized photodiodes that exploit the avalanche effect to achieve higher sensitivity. They are designed with a high reverse bias voltage, which creates an internal electric field strong enough to cause carrier multiplication. This multiplication process results in an avalanche of carriers, amplifying the original photocurrent. APDs are used in applications requiring high sensitivity, such as low-light-level detection and long-range optical communication.

5. **Charge-Coupled Devices (CCDs):** CCDs are sophisticated imaging devices used in digital cameras, scanners, and scientific instruments. They consist of an array of light-sensitive capacitors arranged in a grid pattern. Incident photons generate electron-hole pairs, which are then stored in the capacitors. By sequentially reading out the stored charges, CCDs can create high-resolution images with excellent sensitivity and low noise.

6. **Complementary Metal-Oxide-Semiconductor (CMOS) Image Sensors:** CMOS image sensors are an alternative to CCDs for imaging applications. They are based on CMOS technology, commonly used in digital integrated circuits. CMOS image sensors integrate both the image sensing and signal processing functions onto a single chip. They offer lower power consumption, faster readout speeds, and better on-chip integration compared to CCDs.

These are just a few examples of inorganic semiconductor photodetectors. Researchers and engineers continue to explore new materials, structures, and technologies to develop photodetectors with improved performance, efficiency, and versatility to meet the evolving demands of various applications.

1.2.3 Challenges

A brief description of some challenges associated with inorganic semiconductor photodetectors[23][24]:

1. **Noise:** One of the major challenges in inorganic semiconductor photodetectors is the presence of noise, which can limit the overall sensitivity and performance of the device. Various noise sources, such as thermal noise, shot noise, and dark current noise, can degrade the signal-to-noise ratio. Reducing noise and optimizing the device design and operation are crucial to improving the sensitivity and detection limits of photodetectors.

2. **Spectral Range:** Different applications require photodetectors to operate over specific spectral ranges. Inorganic semiconductor photodetectors have inherent limitations in their spectral response due to the properties of the materials used. Matching the spectral sensitivity of the photodetector to the desired range often requires careful material selection or additional techniques such as spectral filters or heterostructures.

3. **Bandgap Limitations:** The bandgap of inorganic semiconductors dictates the range of photons they can absorb and detect. For certain applications, such as ultraviolet (UV) or infrared (IR) detection, the available materials may not have suitable bandgaps. Overcoming this challenge often involves either the development of new materials or the use of hybrid or composite structures to extend the spectral range of the photodetectors.

4. **Temperature Effects:** Temperature can significantly affect the performance of inorganic semiconductor photodetectors. Changes in temperature can alter the electrical and optical properties of the semiconductor material, leading to variations in sensitivity, response time, and dark current.

Thermal management techniques, such as cooling or temperature compensation circuits, may be necessary to ensure stable and reliable operation of photodetectors.

5. **Manufacturing and Cost:** : Large-scale manufacturing of inorganic semiconductor photodetectors can be challenging, particularly for high-performance or specialized devices. The fabrication processes often involve complex and precise techniques, such as lithography and thin-film deposition. The cost of production, especially for advanced materials or specialized structures, can also be a significant challenge that limits the widespread adoption of certain photodetectors.

6. **Integration and Packaging:** Integrating photodetectors into practical systems and packaging them for specific applications can pose challenges. Proper integration requires addressing issues such as alignment, connectivity, and compatibility with other electronic components. Packaging should ensure protection from environmental factors, mechanical stability, and efficient coupling of incident light to the active area of the photodetector.

Addressing these challenges requires continuous research and development in materials, device design, fabrication techniques, and system integration. Overcoming these obstacles will lead to improvements in the performance, sensitivity, and cost-effectiveness of inorganic semiconductor photodetectors, enabling their broader application in various fields.

1.3 Organic Semiconductor

Organic semiconductors are carbon-based materials with unique electronic properties. They have a narrow energy bandgap, enabling both conducting and insulating behavior. Although their charge carrier mobility is lower than inorganic semiconductors, organic semiconductors offer flexibility for applications in flexible electronics and wearables. They are used in OLEDs, OPVs, OFETs, and organic sensors. Ongoing research aims to improve their charge carrier mobility, stability, and efficiency, driving advancements in flexible electronics, wearable tech, and energy harvesting[**18**][20].

1.3.1 Charge Transport in Organic Semiconductors

Charge transport in organic semiconductors is a fundamental process in organic electronic devices. Unlike inorganic semiconductors, organic semiconductors consist of carbon-based molecules or polymers. Charge transport involves the movement of electrons or holes through the material, contributing to electric current conduction. Understanding charge transport mechanisms is crucial for optimizing device performance and efficiency.[20] The transport of charge carriers in organic semiconductors can be described by several mechanisms:

1. **Band-like Transport:** In some highly ordered organic semiconductors, charge transport can resemble the mechanism observed in inorganic semiconductors. Here, the charge carriers move through energy bands, similar to the valence and conduction bands in inorganic materials. This band-like transport is typically observed in crystalline organic materials with well-defined molecular arrangements, such as small organic molecules in single crystals.

2. **Hopping Transport:** In many disordered or amorphous organic semiconductors, charge transport occurs through a hopping mechanism. In this process, charge carriers move by hopping between localized energy states or molecular sites within the organic material. This mechanism is influenced by the disorder and energetic landscape of the material. Hopping transport is more prevalent in amorphous or polymeric organic semiconductors, where the molecular packing is less ordered.

3. **Trap-Assisted Transport:** In some cases, the movement of charge carriers can be influenced by trap states within the organic semiconductor. Trap states refer to localized energy levels in the material where charge carriers can be temporarily captured. Charge carriers can be thermally excited from these trap states and continue their movement, contributing to the overall charge transport. Trap-assisted transport is particularly significant in disordered organic materials with a high density of trap states.

The choice of organic semiconductor material, molecular structure, and device fabrication techniques can significantly influence the charge transport properties. By engineering the molecular arrangement, crystallinity, and energetic landscape, researchers can enhance the charge carrier mobility and reduce the likelihood of trap states, leading to improved device performance.

Understanding and controlling charge transport in organic semiconductors is a critical aspect of developing efficient organic electronic devices such as organic light-emitting diodes (OLEDs), organic solar cells, and organic field-effect transistors (OFETs). Ongoing research aims to uncover novel materials, device architectures, and processing methods that can enhance charge transport and enable the realization of high-performance organic electronic devices[25].

1.3.2 Types of Organic Photodetectors

Organic semiconductor photodetectors can be classified based on various factors, including operating mechanisms and device structures[19]. Here is a brief description of different classifications of organic semiconductor photodetectors:

1. **Photodiodes:** Organic photodiodes (OPDs) are widely used organic semiconductor photodetectors. They are based on a p-n junction or an interface between different organic materials. Incident light generates electron-hole pairs in the active organic layer, and the resulting photocurrent is measured. OPDs offer advantages such as tunable spectral response, low-cost fabrication, and compatibility with flexible substrates.

2. **Phototransistors:** Organic phototransistors (OPTs) combine the functionality of a photodiode and a transistor. They consist of a photoactive layer between the source and drain electrodes, and incident light modulates the conductivity of the organic material, leading to a change in the transistor's output current. OPTs provide amplification and are suitable for applications requiring high sensitivity.

3. **Photoconductors:** Organic photoconductors (OPCs) are based on materials whose electrical conductivity changes upon light absorption. They can be either bulk or thin-film devices. When illuminated, the absorbed photons create electron-hole pairs, altering the conductivity of the organic material. The change in conductivity is measured as a photocurrent. OPCs are used in various applications, such as imaging sensors and photocopiers.

4. **Organic Avalanche Photodiodes:** Organic avalanche photodiodes (OAPDs) are specialized photodiodes that utilize avalanche multiplication to achieve high gain and sensitivity. They operate under high reverse bias, allowing for electron impact ionization and subsequent multiplication of carriers. OAPDs are suitable for low-light-level detection applications.

5. **Organic Single-Photon Detectors:** Organic single-photon detectors (OSPDs) are designed to detect single photons. They typically utilize a combination of organic and inorganic materials or incorporate quantum dots. OSPDs are used in applications such as quantum cryptography, quantum information processing, and low-light-level imaging.

6. **Organic Hybrid Photo detectors:** Organic hybrid photodetectors combine organic semiconductors with other materials, such as inorganic semiconductors or nano particles, to enhance the device performance. These hybrid structures can exploit the benefits of both organic and inorganic materials, including improved charge transport, increased sensitivity, and extended spectral range.

These are some of the common classifications of organic semiconductor photodetectors. Each type offers unique advantages and is suitable for specific applications. Ongoing research and development in the field of organic semiconductors continue to improve the performance, efficiency, and versatility of these photodetectors, expanding their applications in various opto electronic devices and systems.

1.3.3 Challenges

Organic semiconductor photodetectors have garnered significant attention due to their unique properties and potential for applications such as imaging, sensing, and communication. However, several challenges exist in the development and optimization of organic semiconductor photodetectors[25]. Here is a brief description of some of the key challenges:

1. **Low Quantum Efficiency:**

   One of the primary challenges in organic semiconductor photodetectors is achieving high quantum efficiency. Quantum efficiency refers to the percentage of incident photons that are successfully converted into electrical charges. In many organic materials, the quantum efficiency is limited due to various factors such as low light absorption, inefficient charge generation, and charge recombination processes. Improving the quantum efficiency requires the design and synthesis of organic materials with optimized light-absorbing properties and reduced charge recombination.

2. **Limited Spectral Sensitivity:** Organic semiconductor photodetectors often exhibit limited spectral sensitivity, meaning they may not efficiently detect light across a wide range of wavelengths. The absorption spectra of organic materials are typically broad and can be tuned through molecular engineering, but achieving high sensitivity in both the visible and near-infrared regions remains a challenge. Enhancing the spectral sensitivity requires the development of organic materials with tailored absorption properties or the integration of multiple materials to cover a broader range of wavelengths.

3. **Slow Response Time:** Organic semiconductor photodetectors tend to exhibit slower response times compared to their inorganic counterparts. This slow response is attributed to various factors, including the trap states and energy disorder present in organic materials, as well as the nature of charge transport mechanisms. Improving the response time requires minimizing trap states and optimizing the charge transport properties through the design of materials and device structures. Strategies such as reducing material defects, enhancing charge carrier mobility, and optimizing electrode interfaces can help overcome this challenge.

4. **Stability and Reliability:** Organic materials can be prone to degradation when exposed to environmental factors such as moisture, oxygen, and light. This can lead to a decrease in device performance over time, affecting the stability and reliability of organic semiconductor photodetectors. Developing strategies to improve the stability of organic materials, such as encapsulation techniques and interface engineering, is crucial for ensuring the long-term reliability of photodetectors.

5. **Scalability and Manufacturing:** Organic semiconductor

photodetectors often face challenges related to scalability and manufacturing processes. Achieving uniform and large-area deposition of organic materials can be challenging, especially when using solution-based techniques such as printing or coating. Additionally, ensuring reproducibility and reliability in large-scale production is a significant hurdle that needs to be addressed to enable commercialization and widespread adoption of organic photodetectors.

Addressing these challenges requires interdisciplinary research efforts focused on materials design, device engineering, and understanding fundamental charge transport mechanisms in organic semiconductors. Continued advancements in organic material synthesis, device architecture, and fabrication techniques will pave the way for improved performance, efficiency, and reliability of organic semiconductor photodetectors.

1.3.4 Types of Organic Photodiode

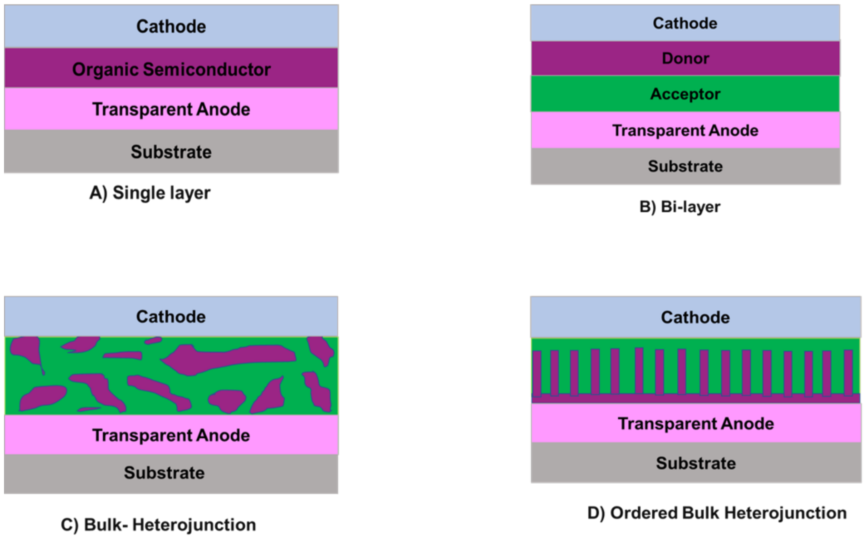
Organic photodiodes (OPDs) are photodetectors that utilize organic materials to convert light into electrical signals. OPDs can be categorized into various types based on their device structure and the arrangement of organic layers as shown Figure 1.4 .[19][25] Here is a brief description of some common types of photodiode-based organic photodetectors:

1. **Single-layer Photodiodes:** Single-layer OPDs, also known as single-layer heterojunction photodiodes, consist of a single organic layer sandwiched between two electrodes. The organic layer typically acts as both the light-absorbing material and the charge transport medium. This simple device structure allows for easy fabrication and can exhibit efficient charge generation and collection. However, single-layer OPDs often suffer from limited spectral sensitivity due to the broad absorption spectra of organic materials.

2. **Bilayer Photodiodes:** Bilayer OPDs consist of two organic layers with different energy levels sandwiched between the electrodes. The absorption layer absorbs the incident light and generates electron-hole pairs, while the charge transport layer facilitates the efficient extraction and collection of charge carriers. Bilayer OPDs can offer improved spectral sensitivity compared to single-layer devices by carefully selecting the light-absorbing and charge transport materials.

3. **Bulk Heterojunction (BHJ) Photodiodes:** BHJ OPDs are constructed using a blend of electron-donor and electron-acceptor materials, forming a bulk heterojunction structure. The blend of materials creates a highly intermixed network of donor-acceptor interfaces, which enhances light absorption and facilitates efficient charge separation. BHJ OPDs often exhibit improved performance due to the increased interfacial area, extended light absorption range, and efficient charge transport pathways.

4. **Ordered Bulk Heterojunction (OBHJ) Photodiodes:** OBHJ OPDs are a specialized type of BHJ photodiodes where the donor and acceptor materials are arranged in an ordered and periodic manner. This is typically achieved through processes such as self-assembly or controlled crystallization. The ordered structure in OBHJ devices enhances charge transport and reduces recombination, leading to improved device performance and higher external quantum efficiency.



A) Single layer

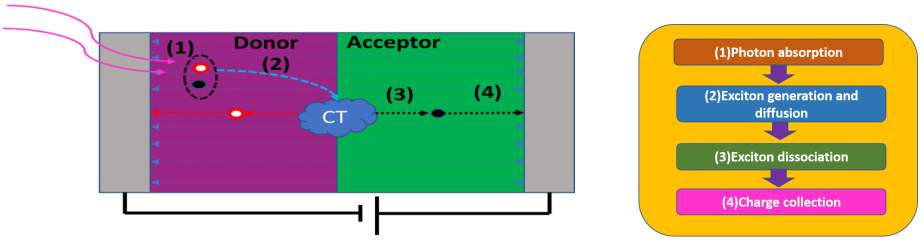
B) Bi-layer

C) Bulk- Heterojunction

D) Ordered Bulk Heterojunction

Fig. 1.4: **Types of The Organic Photodiode**

Each type of photodiode-based organic photodetector offers specific advantages and challenges. The choice of device structure depends on the desired performance metrics, such as spectral sensitivity, response time, and device fabrication considerations. Ongoing research aims to further optimize the design and materials selection for different types of photodiodes, leading to advancements in organic photodetection technology.



((a)) *((b))*

Fig. 1.5: **(a) Working principle of organic photo diode (b) Major points of working of organic photo diode**

Working Principle of Organic Photodiode

An organic photodiode operates by utilizing the fundamental concepts of photon absorption, exciton generation and diffusion, exciton dissociation, and charge collection to convert light into an electrical signal as illustrated in Figure 1.5 [26]. Let's explore the working of an organic photodiode in more detail:

1. **Photon absorption:** When light, consisting of photons, falls on the active organic layer of the photodiode, some photons are absorbed by the organic molecules. The energy of the absorbed photons matches the energy bandgap of the organic material.

2. **Exciton generation and diffusion:** The absorbed photons create excitons, which are electron-hole pairs, in the organic layer. These excitons are bound states where an electron and a hole are strongly correlated. The excitons diffuse within the organic layer due to thermal energy.

3. **Exciton dissociation:** At the interface between the organic layer and the charge-collecting electrode, the bound excitons undergo dissociation. This process separates the electron and the hole, freeing them to move independently.

4. **Charge collection:** The liberated electrons and holes are then collected by the respective electrodes, creating an electrical current. The electrons are collected at the electron-collecting electrode (such as a cathode), while the holes are collected at the hole-collecting electrode (such as an anode). The flow of these charges constitutes the electrical signal generated by the photodiode.

The current equation of a PN junction diode is given by the Shockley diode equation:

$$I = I_S \left(e^{\frac{V}{nV_T}} - 1 \right) \tag{1.1}$$

where,

I : Diode current

I_S: Reverse saturation current

V: Applied voltage across the diode

(n) : Ideality factor

V_T : Thermal voltage (kT/q, where k is the Boltzmann constant, T is the temperature in Kelvin, and q is the elementary charge)

The Shockley diode equation describes the relationship between the diode current and the applied voltage, taking into account factors such as the forward bias region, reverse bias region, and temperature. It is a fundamental equation used to analyze and model the behavior of PN junction diodes[27].

The efficiency of an organic photodiode depends on various factors, including the photon absorption characteristics of the organic material, the ability of excitons to diffuse to the interface, and the effectiveness of exciton dissociation and charge collection processes.

In summary, an organic photodiode operates by absorbing photons, generating and diffusing excitons, dissociating the excitons at the electrode interface, and collecting the resulting free charges to produce an electrical signal.

1.4 Hybrid Photodetectors

Organic-inorganic hybrid photodetectors are a type of photodetector that combines organic and inorganic materials to achieve enhanced performance and functionality. These devices leverage the unique properties of both material classes to create a synergistic effect[21][28]. Here is a brief description of organic-inorganic hybrid photodetectors:

1. **Structure:** Organic-inorganic hybrid photodetectors typically consist of a composite structure where an organic semiconductor layer is integrated with an inorganic material or nanostructures. The organic semiconductor layer absorbs incident light, generating charge carriers, while the inorganic component assists in charge transport, amplification, or energy harvesting.

2. **Benefits of Hybridization:** The combination of organic

and inorganic materials in hybrid photodetectors offers several advantages. Organic semiconductors provide flexibility, solution-processability, and tunable absorption properties over a wide range of wavelengths. Inorganic components, such as nanoparticles or nanostructures, can enhance charge transport, increase carrier mobility, and provide amplification mechanisms like avalanche multiplication.

3. **Charge Transfer and Transport:** One key aspect of organic-inorganic hybrid photodetectors is the efficient transfer and transport of charge carriers between the organic and inorganic materials. The interface between these materials allows for effective charge separation and migration, leading to enhanced photocurrent generation and reduced recombination losses.

4. **Performance Enhancements:** The hybridization of organic and inorganic materials can lead to improved device performance. By leveraging the high carrier mobility and long exciton diffusion lengths of inorganic materials, hybrid photodetectors can achieve faster response times, higher quantum efficiencies, and lower noise levels compared to purely organic devices. The combination of materials with complementary properties allows for the optimization of key parameters such as responsivity, detectivity, and dynamic range.

5. **Applications:** Organic-inorganic hybrid photodetectors find applications in various fields, including imaging, sensing, and energy harvesting. They are used in optoelectronic devices such as photovoltaic cells, photodetector arrays, and light sensors. Hybrid photodetectors offer the versatility to design devices with tailored properties for specific wavelength ranges, enabling applications in areas such as visible light communication, environmental monitoring, and biomedical imaging.

The development of organic-inorganic hybrid photodetectors is an active area of research, focusing on material selection, interface engineering, and device optimization. By combining the advantages of organic and inorganic materials, these hybrid photodetectors aim to overcome the limitations of purely organic or purely inorganic devices, opening up new opportunities for advanced optoelectronic technologies[29][30].

1.5 Review of Past Work

Organic photodiodes (OPDs) offer a promising solution for sensing applications, particularly in the near-infrared (NIR) spectrum. These solution-processed devices are attractive for industrial and medical sensors that require operation in the NIR range while being visible-blind. OPDs provide a solid-state alternative without the need for filters and can be designed with large active areas, enabling the fabrication of lens-free light-barrier and reflective sensors[31].

This paper discussed various approaches to achieve large active area OPDs with NIR sensitivity using both polymers and small molecules as light absorbers. By optimizing the layer stacks to the properties of solution-processed semiconductors, the researchers demonstrated OPDs with bulk heterojunctions that achieved a minimum external quantum efficiency peak of over 40% in the NIR range and a rectification ratio of approximately 105, meeting the requirements of industrial sensing applications[32].

Overall, the study highlighted the potential of highly NIR-sensitive OPDs using polymeric and small molecule absorbers in bulk heterojunction structures, emphasizing the importance of optimizing the diode stack based on material properties. These OPDs could find applications in light barrier systems or reflective sensors as an alternative to traditional solid-state solutions[33].

Furthermore, the review on recent progress in organic NIR photodiodes revealed the advantages and challenges associated with these devices. Organic semiconductors offer tunability of optical and electronic properties through molecular design, thin film flexibility, and ease of processing. The development of efficient low-bandgap photovoltaic materials has enabled the realization of both panchromatic and narrowband organic NIR photodiodes[34].

To achieve higher detectivity and enhance responsivity while suppressing dark current, optimization of the photoactive layer thickness, morphology, and the introduction of efficient charge transport layers (CTLs) are crucial. The dominance of fullerene derivatives as electron acceptors in organic photodiodes calls for the development of novel non-fullerene acceptors with strong absorption and finely-tuned energy levels[**29**].

The adoption of highly conductive non-metal materials as electrodes and the consideration of stability issues are important factors to be addressed in NIR photodiodes. Ternary blend organic photodiodes, non-fullerene acceptors with low intrinsic free carrier density, and protective filter layers can contribute to improved device performance and stability[35].

Furthermore, within the domain of photovoltaic energy conversion, hybrid inorganic/organic devices offer a promising alternative to standard photovoltaic systems. These devices utilize metal oxide nanostructures like titanium dioxide (TiO2) and zinc oxide (ZnO) as electron transporters, which are cost-effective, non-toxic, biocompatible, and possess suitable charge transport properties. The two main categories of hybrid solar cells are dye-sensitized solar cells (DSSCs) and bulk heterojunction (BHJ) solar cells. DSSCs use a nanostructured metal oxide electrode sensitized by a molecular dye, while BHJ cells employ conjugated polymer/metal oxide interfaces to generate photocurrent. Both approaches have shown steady improvement in performance over the years, with solid-state DSSCs reaching efficiencies of up to 6% and hybrid BHJs achieving just over 3%.[36][37]

To further enhance the efficiency and competitiveness of these hybrid devices, new strategies are being explored. One such strategy involves incorporating conjugated polymers to extend the light-harvesting properties of solid-state DSSCs, while optically active dyes can broaden the photoresponse of hybrid BHJs. Notably, there is a trend of convergence between DSSC and BHJ approaches, leading to the development of mixed concepts that combine the advantages of both. This convergence holds the potential for the realization of low-cost hybrid devices for efficient photovoltaic energy conversion in the near future. Recent research has demonstrated that the incorporation of a near-infrared absorbing squaraine dye, TBU-SQ, in a polymer solar cell based on P3HT and PC70BM improves light harvesting efficiency and enhances the power conversion efficiency (PCE) from 3.47% to 4.55%. Furthermore, the PCE can be further increased to 5.15% by using a thermally annealed blend film of P3HT:TBU-SQ:PC70BM, which broadens the absorption wavelength range and improves charge transport, leading to enhanced light harvesting and overall device performance. These findings highlight the potential of TBU-SQ as a promising sensitizer for boosting the PCE of polymer-based solar cells[38].

In summary, organic photodiodes hold great promise for NIR sensing applications, offering advantages such as versatility in material variety, low-cost manufacturing, lightweight, flexibility, and scalability. The advancement of material design, interfacial engineering, and device optimization has led to significant progress in achieving high-performance NIR photodiodes. However, further research and development are needed to overcome challenges such as dark current suppression, material stability, and device integration, paving the way for their practical application in various fields[31].

1.6 Objectives of this Work

This study focuses on the fabrication and enhancement of near-infrared (NIR) hybrid photodetectors while leveraging the advantages of soluble processing organic polymers and small molecules. The primary objective is to achieve improved efficiency for healthcare applications. The main emphasis is placed on modifying and investigating the photoactive layer for its effective utilization in NIR photodetection devices. Specifically, the study utilizes P3HT as conjugated organic polymers, Squaraine dye as an organic small molecule, and ZnO as the inorganic semiconductor. The notable highlights of this research comprise the following:

1. Investigation of the chemical structure and properties of ZnO, an inorganic semiconductor, as well as P3HT, a conjugated polymer, and Squarine Dye, a small molecule. This exploration facilitates the fabrication process of near-infrared (NIR) hybrid organic photodetectors.

2. Development of ZnO/P3HT UV-Vis hybrid photodetectors: This involves creating a dual-wavelength tuned photodetector capable of detecting near-ultraviolet (UV) light and visible light by utilizing ZnO and P3HT.

3. Fabrication of ZnO/P3HT:Squarine Dye NIR hybrid photodetectors: The aim of this step is to enhance the performance of the photodetector in the NIR region. This is achieved by employing simple and cost-effective solution processing techniques to blend conjugated polymer (CP) with small molecule (SM). The resulting hybrid photodetector is based on a ZnO/P3HT:Squarine Dye blend, with the goal of achieving a good rectification ratio and a desired photo sensitivity.

1.7 Organization of the Thesis

1. **Chapter 1** This chapter provides an overview of electronics, focusing on inorganic and organic semiconductors. It explores the significance of hybrid photodetectors, which involve the combination of organic and inorganic semiconductors. Additionally, it highlights the main research theme presented in this thesis, which will be discussed extensively.

2. **Chapter 2** The work in this chapter involves discussing the material and deposition process employed. It includes an examination of various techniques used for characterizing the structural and optical properties of the devices. The thesis also provides a brief overview of these techniques.

3. **Chapter 3** This chapter focuses on the fabrication and characterization of a hybrid photodetector using organic-inorganic materials, specifically ZnO and P3HT. The primary objective is to study the optical response of the photodetector in relation to different wavelengths. The chapter will delve into the details of the fabrication process and discuss the characterization techniques employed to evaluate the device performance.

4. **Chapter 4** This chapter focuses on the fabrication of a hybrid photodetector using ZnO/P3HT: Squarine dye. The primary objective of this work is to improve the performance of the detector in the near-infrared (NIR) region. To achieve this, the study employs simple and cost-effective solution processing techniques. The chapter will provide detailed information about the fabrication process and highlight how these techniques contribute to enhancing the detector's performance in the desired NIR range.

5. **Chapter 5** This chapter serves as the culmination of the thesis, presenting the conclusion of the research work conducted. It also provides a brief overview of the future prospects and potential areas for further investigation in this field

Chapter 2

Materials, Experimental Methods and Characterization

In this chapter, we provide a concise introduction to the materials used in the research presented. Additionally, we outline various techniques related to the fabrication and characterization of the devices. The chapter covers the fabrication process of the devices, along with an explanation of the characterization tools employed in the study.

2.1 Material

Choosing the right material is crucial to meet the criteria for efficient device fabrication. The material properties directly influence the physics of the device. Therefore, it is essential to thoroughly investigate the optical and electrical characteristics of the material before applying it. Only materials that meet the necessary conditions of energy bandgap, energy levels, and whether they act as donors or acceptors can be selected for the active layer. Other properties such as surface tension, solubility, melting point, and evaporation are significant when employing solution-based fabrication techniques. In the case of hybrid photodetector design, it is vital to choose a material capable of both exciton splitting and charge transfer. All materials used in the study are employed as received without any additional processing or purification steps.

2.1.1 Indium Tin Oxide (ITO)

In this study, all the devices were fabricated on glass substrates coated with Indium Tin Oxide (ITO) or tin-doped indium oxide. ITO-coated glass is a commonly used substrate due to its flatness, rigidity, and transparency in the visible and near-infrared spectral range, which is of interest for the study. ITO is widely recognized as one of the most effective transparent conducting oxides, possessing high electrical conductivity and optical transparency. It also exhibits a relatively high work function of approximately 4.8 eV. Another advantage of ITO is its exceptional atmospheric stability and insolubility, allowing it to be used in wet processing conditions during cleaning and spin coating. The manufacturer's specifications for the ITO-coated glass include a sheet resistance ranging from 15 to 25 Ω, an ITO layer thickness between 80 and 120 nm, and a transmittance greater than 78%

In summary, ITO serves as an ideal electrode material in hybrid photodetector fabrication due to its high transparency, excellent electrical conductivity, low resistivity, compatibility with other materials, and stability. These properties contribute to the efficient collection of photo-generated charges, improved device sensitivity, and overall performance of the photodetector[39][40].

2.1.2 Zinc oxide (ZnO)

ZnO is a versatile compound with a wide range of applications due to its unique properties. Here is a brief description of ZnO and its important properties[41][42]:

1. **Chemical Composition:**

   Zinc oxide is an inorganic compound composed of zinc (Zn) and oxygen (O). Its chemical formula is ZnO.

2. **Crystal Structure:** ZnO crystallizes in the wurtzite structure, which is a hexagonal lattice arrangement as illustrated in Figure 2.1. The crystal structure contributes to its unique properties and makes it suitable for various applications.

3. **Optical Properties:** ZnO exhibits a wide bandgap of approximately 3.37 eV, which corresponds to its strong ultraviolet (UV) absorption. It is transparent in the visible region of the electromagnetic spectrum, making it useful for UV filters and transparent conducting electrodes.

4. **Electrical Properties:** ZnO is a semiconductor with excellent electrical properties. It has a high electron mobility and a large exciton binding energy, making it suitable for electronic and optoelectronic devices such as transistors, light-emitting diodes (LEDs), and solar cells.

5. **Piezoelectric Properties:** ZnO possesses piezoelectric properties, meaning it can generate an electric charge in response to applied mechanical stress or deformations. This property makes ZnO useful in sensors, actuators, and energy harvesting devices.

6. **Thermal Stability:** ZnO exhibits good thermal stability, allowing it to withstand high temperatures without significant degradation. This property is advantageous for applications in high-temperature environments.

7. **Antibacterial Properties:** ZnO has been found to possess antibacterial properties, making it useful for various medical and healthcare applications, such as wound dressings, antibacterial coatings, and personal care products.

8. **Environmental Compatibility:** ZnO is considered environmentally friendly and non-toxic, which is advantageous for applications in areas such as green electronics, sustainable energy, and biomedical devices.

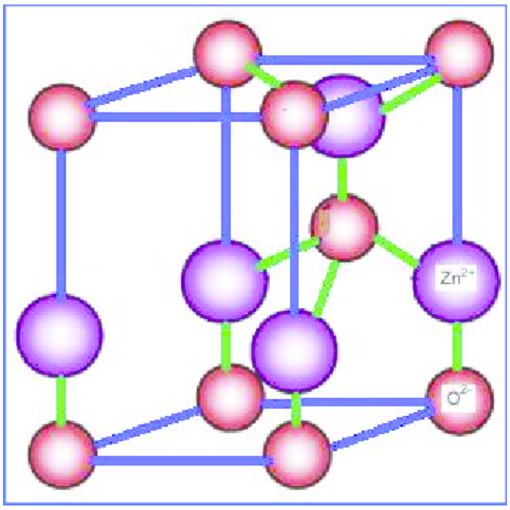


Fig. 2.1: **Wurtzite structure of ZnO[43]**

ZnO's unique combination of properties, including its wide bandgap, excellent electrical characteristics, piezoelectricity, thermal stability, antibacterial properties, and environmental compatibility, make it a highly versatile material for a wide range of applications in electronics, optoelectronics, sensors, energy devices, and biomedical fields. Ongoing research continues to explore new applications and optimize the properties of ZnO for various technological advancements[44].

2.1.3 ZnO Nanostructures

Zinc oxide (ZnO) nanostructures refer to nanoscale architectures composed of zinc oxide material. These nanostructures exhibit unique properties and have garnered significant attention due to their wide range of applications. Here is a brief description of ZnO nanostructures[45][46]:

1. **Nanowires:** ZnO nanowires are elongated structures with diameters typically ranging from a few nanometers to several hundred nanometers and lengths extending up to several micrometers. These one-dimensional nanostructures possess a high aspect ratio and a large surface-to-volume ratio, making them suitable for applications such as nanoscale electronics, sensors, and optoelectronic devices.

2. **Nanorods:** ZnO nanorods are similar to nanowires but typically have a larger diameter. They exhibit rod-like shapes with lengths varying from several hundred nanometers to a few micrometers. Nanorods possess unique optical and electronic properties, making them suitable for applications in solar cells, photocatalysis, and gas sensors.

3. **Nanoparticles:** ZnO nanoparticles are small, discrete particles with sizes typically ranging from a few nanometers to tens of nanometers. They exhibit a variety of shapes, including spherical, hexagonal, and rod-like. ZnO nanoparticles are utilized in various fields such as cosmetics, pigments, antibacterial agents, and photocatalysis.

4. **Nanosheets:** ZnO nanosheets are two-dimensional nanostructures with a thin, planar geometry. They possess a high surface area, which is advantageous for applications such as gas sensing, photocatalysis, and energy storage devices.

5. **Nanocomposites:** ZnO nanostructures can also be incorporated into nanocomposites, where they are combined with other materials to achieve enhanced properties or specific functionalities. For example, ZnO nanowires or nanoparticles can be integrated into polymers or other matrices to create hybrid materials with improved mechanical, electrical, or optical properties.

ZnO nanostructures exhibit unique properties derived from their nanoscale dimensions, such as quantum confinement effects, increased surface area, and improved optical and electronic properties. These properties make them promising candidates for a wide range of applications, including electronics, optoelectronics, photonics, sensors, energy devices, catalysis, and biomedical applications. Ongoing research aims to further optimize the synthesis methods, control the size and shape of nanostructures, and explore novel applications for ZnO nanostructures.

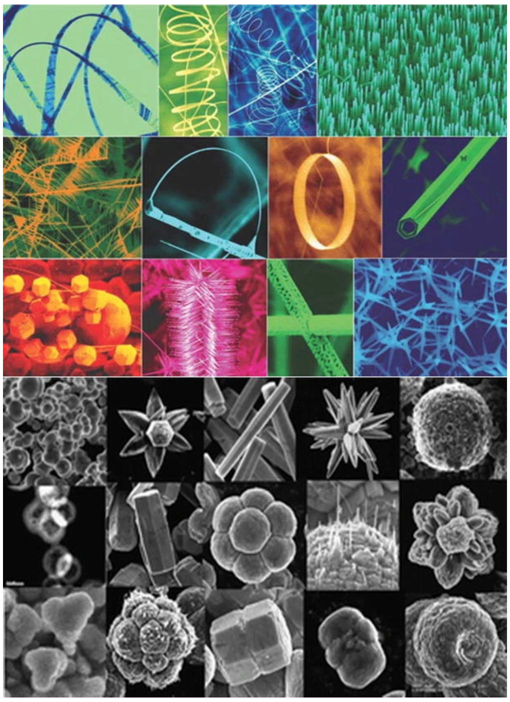


Fig. 2.2: **Various Morphologies of ZnO Nanostructures[47]**

ZnO Nano Structures Synthesis Techniques

The optoelectronic and sensing properties of ZnO depend significantly on the morphologies, defect states, and crystallinity of the nanostructures. Extensive efforts have been devoted to obtaining highly crystalline ZnO nanostructures with diverse morphologies, including nanorods, nanoplates, nanowires, nanoflowers, and tetrapods. The synthesis techniques for ZnO nanostructures can be broadly classified into two categories: gas-phase synthesis and liquid-phase synthesis. Gas-phase synthesis encompasses various techniques such as chemical vapor deposition (CVD), metal-organic chemical vapor deposition (MOCVD), physical vapor deposition (PVD), pulsed laser deposition (PLD), molecular beam epitaxy (MBE), electron beam deposition, and organometallic vapor epitaxy (OMPVE)[48].

Among physical vapor deposition techniques, thermal evaporation is one method used to deposit different types of ZnO nanostructures. In this process, the target materials are heated to their evaporation temperature, resulting in the formation of thin films or nanostructures on the substrate. However, there is a notable risk of introducing catalysts and impurities into the ZnO lattice during the deposition process.

On the other hand, the chemical vapor deposition (CVD) method is a well-established technique known for its ability to achieve excellent crystallinity, uniformity, and control over defect density. In a basic CVD system, a vacuum chamber, precursor gases, and substrate heaters are utilized. The chemical reactions occur near or at the heated substrate, typically at temperatures ranging from 200°C to 1600°C, leading to the growth of highly crystalline and uniform thin films. CVD offers advantages such as excellent coverage and the ability to coat substrates with different features. However, it has limitations, including low product yield and a restricted choice of substrates.

Gas phase deposition techniques, including CVD, thermal evaporation, and MBE, can produce highly crystalline thin films and a variety of nanostructures. However, these techniques require high vacuum pressures and high temperatures, leading to increased complexity and costs in device fabrication. Additionally, they are often not compatible with flexible organic substrates.

In contrast, liquid phase deposition techniques, such as spray pyrolysis, sol-gel technique, hydrothermal growth, and electrospinning, offer advantages over gas phase synthesis. These techniques provide scalability, low production cost, and the ability to synthesize materials at lower temperatures (below 200°C). Hydrothermal growth, in particular, has gained attention due to its ease of processing and the ability to achieve various nanostructures by adjusting growth parameters and precursor solutions[49].

2.1.4 Hydrothermal Synthesis of ZnO Nano Structures

Researchers have shown considerable interest in wet chemical methods for several reasons, such as their compatibility with flexible organic substrates, reduced hazards, and the absence of a metal catalyst. These advantages facilitate the seamless integration of the obtained nanostructures with established silicon technology. Wet chemical methods involve various chemical reactions in reversible equilibrium, driven by the minimization of free energy within the growth environment. Among the deposition techniques, the hydrothermal technique is particularly favored because it enables the production of a wide range of nanostructures and offers precise control over point defects. These defects play a significant role in determining the optoelectronic properties of ZnO. Notably, the presence of mid-gap defect states allows ZnO nanostructures to harness visible light for photocatalytic applications, even without the need for doping with transition metals[42][50]. The synthesis of ZnO nanostructures through the hydrothermal process involves the following sequential steps:

1. **Step 1:** The substrate is coated with a thin layer of ZnO nanoparticles, which serve as seeds for the growth of ZnO nanowires. This deposition can be achieved using techniques such as sputtering, spin coating, or other thin film deposition methods.

2. **Step 2:**The seed layer is then subjected to annealing at high temperatures (ranging from 180°C to 250°C). This annealing process enhances the crystallinity and orientation of the ZnO nanoparticles.

3. **Step 3:** An aqueous precursor solution is prepared, consisting of alkaline reagents (e.g., NaOH, KOH, hexamethylenetetramine, or HMTA) and zinc salts (e.g., $ZnCl_2$, $ZnSO_4$, $Zn(NO_3)_2$). The alkaline solution provides OH^- ions, while the zinc salts act as a source of Zn^{2+} ions required for the growth of ZnO nanowires.

4. **Step 4:**The substrate coated with the seed layer is immersed in the precursor solution and maintained at a fixed temperature and pressure for a specified duration of time. This allows the growth of ZnO nanowires to take place.

5. **Step 5:** Following the growth process, the as-grown samples are rinsed with deionized water and subsequently dried in ambient air.

These steps collectively form the hydrothermal process for synthesizing ZnO nanostructures.

The growth mechanism of ZnO nanorods can be described as follows: In the wurtzite structure of ZnO, the $\pm(0001)$ planes represent high-energy polar surfaces, consisting of either Zn^{2+} or

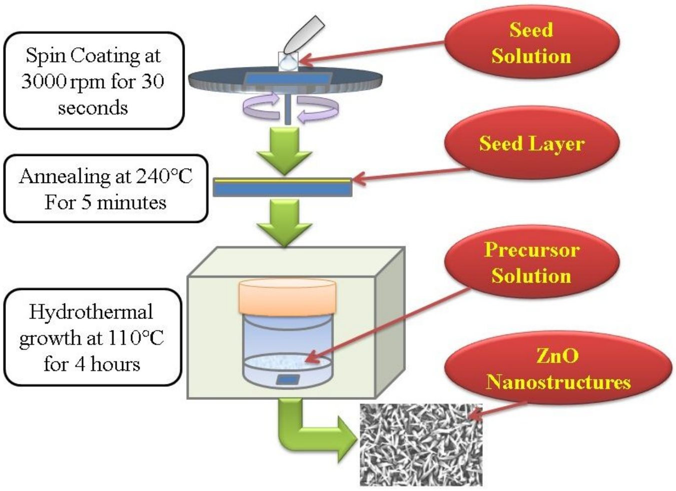


Fig. 2.3: **Schematic representation of the growth of ZnO nanostructures**

OH^-. When the ZnO nucleus forms, OH^- ions preferentially adsorb onto the polar planes to minimize surface energy. Consequently, the surface polarity is inverted, transforming the OH^--terminated plane into a Zn^{2+}-terminated plane, and vice versa. This process repeats over time, leading to rapid growth of ZnO along the c-axis, which exposes nonpolar facets such as $(1\bar{1}00)$ and $(2\bar{1}\bar{1}0)$. As a result, ZnO nanorod-like structures form due to the preferential growth in a specific direction. The hydrothermal technique is highly versatile and allows for the utilization of different surfactants to obtain various types of nanostructures[46]. Additionally, different salts can be introduced into the precursor solution to achieve doped ZnO nanostructures.

$$Zn^{2+} + 2OH^- \longleftrightarrow Zn(OH)_2 \tag{2.1}$$

$$Zn(OH)_2 + 2OH^- \longleftrightarrow [Zn(OH)_4]^{2-} \tag{2.2}$$

$$[Zn(OH)_4]^{2-} \longleftrightarrow ZnO_2^{2-} + 2H_2O \tag{2.3}$$

$$ZnO_2^{2-} + H_2O \longleftrightarrow ZnO + 2OH^- \tag{2.4}$$

$$ZnO + OH^- \longleftrightarrow ZnOOH^- \tag{2.5}$$

During the hydrothermal growth, the following reactions occur in the precursor solution.

The commonly employed reagents for hydrothermal growth, namely HMTA and zinc nitrate, are utilized in the synthesis of ZnO nanostructures. In the case of using HMTA as an alkali reagent, the following reactions take place:

$$(CH_2)_6N_4 + 4H_2O \longleftrightarrow (CH_2)_6N_4 - 4H^+ + 4OH^- \tag{2.6}$$

$$(CH_2)_6N_4 + 6H_2O \longleftrightarrow 6HCHO + 4NH_3 \tag{2.7}$$

$$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^- \tag{2.8}$$

$$Zn^{2+} + 4NH_3 \longleftrightarrow Zn[(NH_3)_4]^{2+} \tag{2.9}$$

$$Zn^{2+} + 2OH^- \longleftrightarrow Zn(OH)_2 \tag{2.10}$$

$$Zn(OH)_2 \longleftrightarrow ZnO + H_2O \tag{2.11}$$

In contrast to growth in an alkali solution, where OH^- ions are supplied by the presence of H_2O molecules, HMTA serves as a pH buffer, ensuring a constant provision of OH^- ions in the precursor solution (eq. 2.1). Additionally, the hydrolysis of HMTA generates ammonia and formaldehyde (HCHO) within the solution. The decomposition of HMTA depends on the pH and temperature conditions. Ammonia plays two significant roles: firstly, it maintains a consistent supply of OH^- ions, and secondly, it forms a complex with Zn^{2+} ions, facilitating a timely and stable delivery of Zn^{2+} ions. Subsequently, the Zn^{2+} ions react with the OH^- ions, leading to the formation of $Zn(OH)_2$. However, $Zn(OH)_2$ is thermodynamically unstable and undergoes a transformation to ZnO . As depicted in Figure 2.4 , HMTA not only accelerates growth along the c-axis but also adheres to the nonpolar facets, impeding lateral growth and enabling the access of ZnO molecules to the (0001) plane. This promotes the growth of ZnO nanorods with high aspect ratios[48][49].

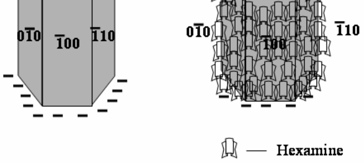


Fig. 2.4: **Schematic showing role of HMTA as a capping agent to promote 1-D growth [51]**

2.1.5 Poly(3-hexylthiophene) (P3HT)

Poly(3-hexylthiophene) (P3HT) is a semiconducting polymer that has garnered significant interest in the field of organic electronics. It possesses unique properties that make it well-suited for a range of applications in devices such as organic solar cells and organic field-effect transistors (OFETs)[52][53].

P3HT is composed of repeating units containing a thiophene ring with hexyl side chains attached to every third carbon atom as shown in the Figure 2.5. This specific molecular structure imparts several important properties to P3HT[54][55]:

1. **Semiconducting Behavior:** P3HT is a conjugated polymer with a relatively low bandgap, allowing it to absorb light in the visible region of the electromagnetic spectrum. This property enables efficient light absorption and promotes the generation of excitons (electron-hole pairs) for use in photovoltaic devices.

2. **Charge Transport:** P3HT exhibits favorable charge transport characteristics, facilitating the movement of electrons and holes along the polymer chain. This property is crucial for achieving efficient charge carrier mobility and enables the effective operation of electronic devices based on P3HT.

3. **Film-Forming Capability:** P3HT can be processed into thin films using methods like spin-coating or drop-casting. It forms well-organized, self-assembled structures, which are vital for achieving high-performance devices and facilitating charge transport within the polymer film.

4. **Tunable Absorption Properties:** The absorption properties of P3HT can be tuned by modifying its chemical structure or blending it with other materials. This adjustability allows for optimization of device performance and enables matching of the polymer's absorption spectrum with the solar spectrum in photovoltaic applications.

5. **Environmental Stability:** P3HT exhibits good stability under ambient conditions, making it suitable for device fabrication and operation in real-world environments. This stability contributes to the longevity and reliability of P3HT-based devices.

6. **Energy Levels:** Regarding its energy levels, P3HT has a highest occupied molecular orbital (HOMO) level that typically ranges from -5.2 eV to -5.5 eV, and a lowest unoccupied molecular orbital (LUMO) level that falls between -3.3 eV and -3.6 eV. The bandgap of P3HT, which represents the energy difference between the HOMO and LUMO levels, is typically in the range of 1.9 eV to 2.0 eV.

These important properties of P3HT have made it a widely studied and utilized material in the field of organic electronics. Researchers continue to explore its potential in various applications and are working on enhancing its performance through material modifications, interface engineering, and device optimization[56][57][58].

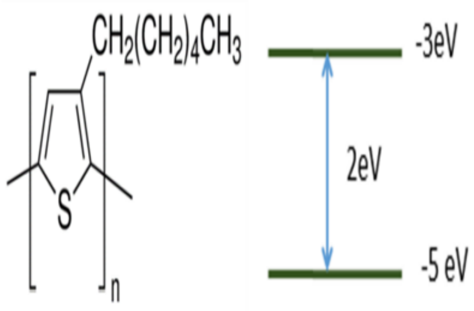


***Fig. 2.5:* Chemical structure and energy band diagram of P3HT [59]**

2.1.6 Squaraine Dye

Squaraine dyes are a class of organic dyes that are widely recognized for their unique properties and have found applications in various fields, including NIR hybrid photodetectors.

One of the key properties of squaraine dyes is their strong absorption in the near-infrared (NIR) region of the electromagnetic spectrum. This characteristic makes them highly suitable for applications that require detection or sensing of NIR light. By fine-tuning the chemical structure of squaraine dyes, their absorption wavelength can be tailored to match specific requirements, enabling efficient utilization of NIR radiation[60][61].

Squaraine dyes exhibit a high molar extinction coefficient, which indicates their ability to strongly absorb light. This high

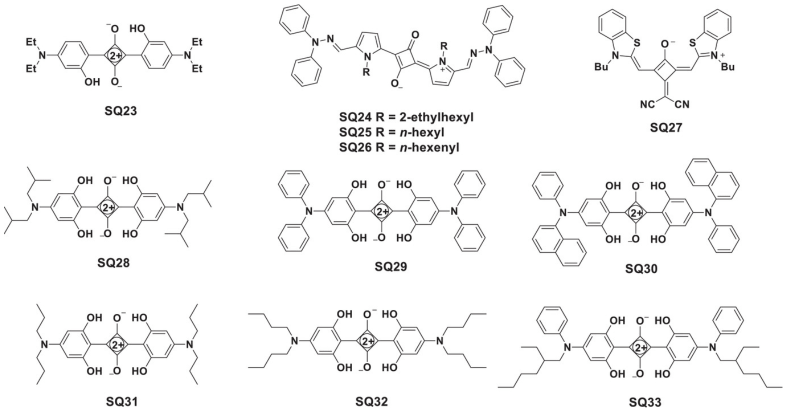


Fig. 2.6: **Squaraine Dyes for Photovoltaic and Biomedical Applications[62]**

absorbance is advantageous in hybrid photodetectors as it enhances the sensitivity and responsiveness of the device to NIR light. Squaraine dyes are known for their efficient energy transfer, allowing for effective conversion of incident photons into electrical signals[63].

Another significant property of squaraine dyes is their chemical stability. This stability ensures the long-term functionality and reliability of the dye in various applications, including NIR hybrid photodetectors[64].

In NIR hybrid photodetectors, squaraine dyes are incorporated as the active material for light absorption and charge generation. When exposed to NIR light, the squaraine dye molecules absorb photons and generate charge carriers (electrons and holes), which can then be collected and converted into electrical signals by the detector. This mechanism enables the detection and measurement of NIR radiation, opening up opportunities for applications such as telecommunications, night vision, and biomedical imaging.

In summary, squaraine dyes possess strong absorption in the NIR region, high molar extinction coefficient, chemical stability, and are utilized in NIR hybrid photodetectors for their efficient light absorption and charge generation properties[65][66].

2.1.7 Silver (Ag)

The implementation of Ohmic contacts in ZnO/P3HT based devices involves the utilization of the noble metal Ag as an electrode. Ag possesses a work function in the range of approximately 4.20 eV to 4.78 eV. To create these contacts, Ag is deposited onto the device using the physical vapor deposition technique, which involves heating the metal to its melting point of 962 °C

2.2 Thin Film Deposition Techniques

2.2.1 Spin Coating

Spin coating is a commonly used technique for depositing thin films onto a substrate. A liquid solution or suspension is dispensed onto the substrate, which is then rapidly spun. Centrifugal force spreads the liquid evenly, and as the solvent evaporates, a thin film forms. The process is adjustable to control film thickness. Spin coating is cost-effective, compatible with various materials, and provides uniform and smooth films. However, it is best suited for thin films on flat substrates and has limitations in film thickness and substrate surface.

In summary, spin coating is a widely used technique for depositing thin films onto substrates. It involves the application of a liquid solution or suspension, which is then spread out uniformly through rapid spinning. Spin coating offers simplicity, cost-effectiveness, and compatibility with various materials, making it a popular choice for thin film deposition in many applications

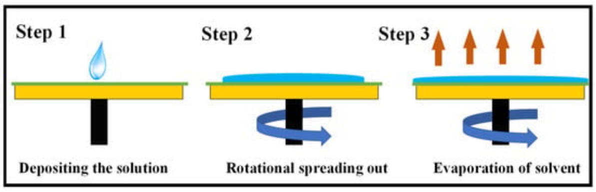


Fig. 2.7: **Schematic of Spin Coating**

2.2.2 Physical vapor deposition (PVD)

Deposition of electrodes using physical vapor deposition (PVD) is a widely used technique in the fabrication of electronic devices. PVD involves the deposition of thin films of materials onto a substrate by the process of physical vaporization and subsequent condensation.

The PVD process typically starts with a solid source material, often in the form of a metal or alloy, known as the target. The target material is placed in a vacuum chamber, and the substrate onto which the deposition will occur is positioned in close proximity. The chamber is then evacuated to a low-pressure environment to minimize gas interactions and impurities.

The target material is heated using various methods such as resistive heating, electron beam evaporation, or sputtering. As the target is heated, atoms or molecules are vaporized from its surface. These vaporized species then travel in straight paths, colliding with gas molecules and the substrate surface. Upon collision, the vaporized material condenses and forms a thin film on the substrate, effectively depositing the electrode material.

PVD offers several advantages for electrode deposition:

1. **Precise Control:** PVD allows for precise control over the deposition process, including film thickness, composition, and morphology. This control is crucial in achieving desired device performance and ensuring uniformity across large-area substrates.

2. **Versatility:** PVD can be utilized for depositing a wide range of materials, including metals, alloys, and even organic materials. This versatility enables the deposition of electrodes with diverse electrical and optical properties to suit specific device requirements.

3. **High Purity:** The vacuum environment in PVD minimizes the presence of impurities, leading to high-purity film deposition. This purity is essential for maintaining device performance, preventing unwanted reactions, and ensuring long-term stability.

4. **Adhesion and Conformality:** PVD deposition generally provides good adhesion between the deposited film and the substrate, promoting strong electrical contact. It also offers excellent conformality, allowing for the coating of complex substrate geometries and three-dimensional structures.

5. **Scalability:** PVD techniques are scalable to various production levels, from laboratory-scale research to industrial-scale manufacturing. This scalability makes PVD suitable for both small-scale device fabrication and large-scale production processes.

Overall, the deposition of electrodes using PVD is a versatile and precise technique that plays a critical role in the manufacturing of electronic devices. By providing control over film properties and enabling the deposition of high-quality thin films, PVD

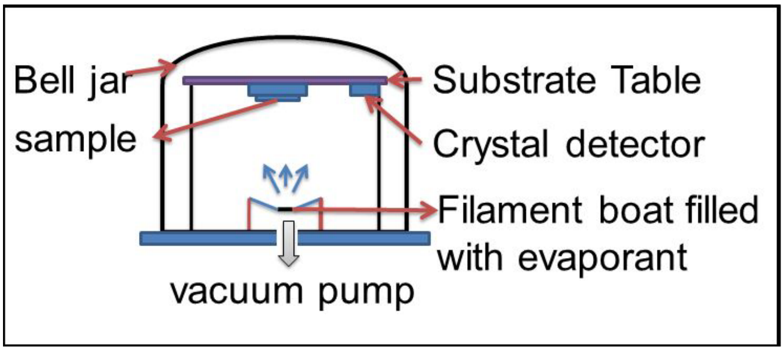


Fig. 2.8: **Schematic of physical vapor deposition**

contributes to the development of efficient and reliable electronic devices across various fields, including semiconductors, optoelectronics, and energy conversion systems.

2.3 Thin Film and Device Characterization Techniques

2.3.1 UV-Vis absorption spectroscopy

UV-Vis absorption spectroscopy is an analytical technique that provides information about the absorption properties of a substance in the UV and visible regions of the electromagnetic spectrum. It involves the interaction of light with a sample, causing electronic transitions within the molecules. The instrument used includes a UV-Vis light source, monochromator, sample holder, and detector. The resulting absorption spectrum reveals energy levels and electronic transitions, allowing the identification of functional groups or compounds. UV-Vis spectroscopy is widely applied in chemistry, biochemistry, pharmaceuticals, and materials science for quantitative analysis, studying reactions, identifying substances, and analyzing sample purity.

The Beer-Lambert law establishes a direct relationship between the absorbance of a solution and the concentration of the absorbing species, as well as the path length. This principle can also be applied to thin films, where the path length is equivalent to the film's thickness. According to this law, the transmitted light's intensity (I) can be expressed as follows:

$$I = I_0 \exp(-\alpha t) \tag{2.12}$$

Here,I_o is the incident light intensity, α is the absorption coefficient, and t signifies the thickness of the film.

In summary, UV-Vis absorption spectroscopy is an important analytical technique that utilizes the absorption of UV and visible light by molecules to provide valuable information about their electronic transitions and properties. It is a versatile and widely used method for qualitative and quantitative analysis in various scientific disciplines.

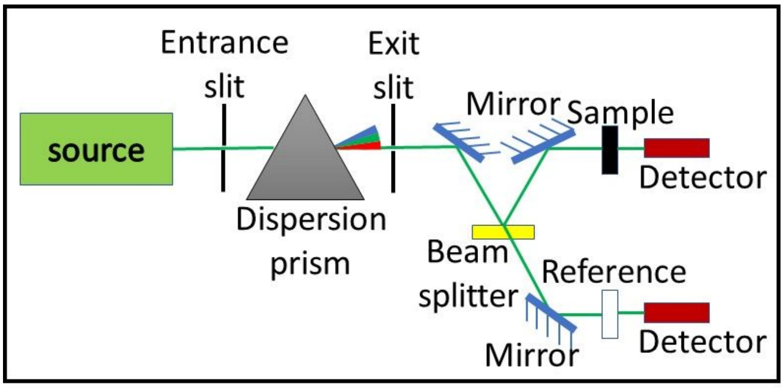


Fig. 2.9: **Experimental set-up:UV-Vis absorption spectroscopy**

2.3.2 Field-Emission Scanning Electron Microscopy

FE-SEM, which stands for Field-Emission Scanning Electron Microscopy, is an electron microscopy technique used to capture high-resolution images of the surface of nanostructures. It operates without physical contact and does not cause any damage to the samples. The technique involves an electron gun that generates a focused beam of high-energy electrons. This beam is directed and scanned over the surface of the nanostructures. When the electrons interact with the surface atoms, various signals are generated, providing information about the topography and chemical composition of the material.

These signals include:

1. **Secondary electrons (SE):** These electrons are used to obtain images of the nanostructure's surface.

2. **Backscattered electrons (BSE):** They are utilized to determine crystal structures and orientation.

3. **Photons:** Characteristic X-rays are emitted, which are employed for elemental analysis.

4. **Visible light (cathodoluminescence, CL):** It provides information about the luminescent properties of the material.

5. **Heat:** The interaction between electrons and the surface also generates heat.

In a typical FE-SEM system, an electron beam is emitted from an electron gun equipped with a tungsten filament cathode. Tungsten is preferred due to its high melting point and low vapor pressure, making it suitable for electron emission. The anode, positively charged with respect to the filament, attracts the electrons, causing them to accelerate towards it. The electron beam passes through a multi-hole aperture, with a standard aperture size of 30 μm. Condenser lenses are used to control the demagnification. The electron beam, focused to a diameter of 1-10 nm, is directed onto the specimen using an objective lens. A scan coil enables the beam to be scanned across the sample's surface. The emitted electrons are collected by a detector and converted to voltage, forming a two-dimensional density distribution of detected electrons, which generates the SEM image.

In the current study, the FESEM Supra55 Zeiss system was employed to investigate the morphology, lengths, sizes, and orientations of ZnO nanostructures. The characterization was performed at an acceleration voltage of 5-10 kV and a working distance of 1-10 mm. For cross-sectional SEM images, the samples were scratched at the backside using a diamond pen and then cracked. To minimize charging effects during SEM measurements, the samples were attached to an SEM stub using carbon tape and coated with a 2 nm Au film.

Figure 2.10 depicts the schematic diagram of the FESEM system utilized in the study.

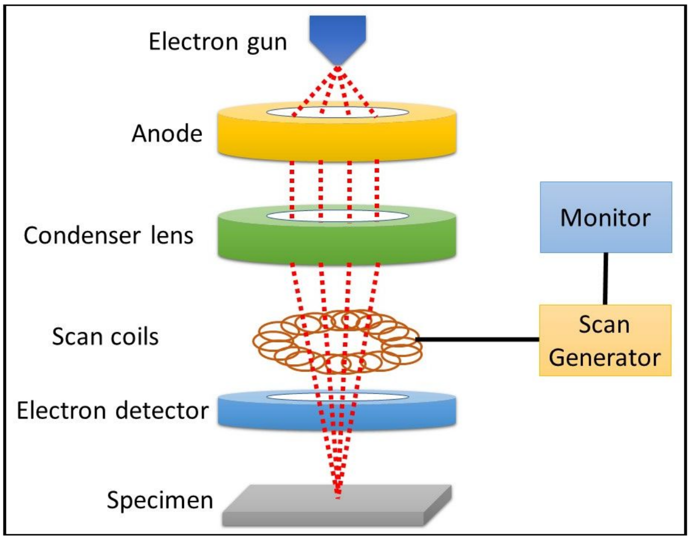


Fig. 2.10: **Schematic diagram of FESEM**

2.3.3 Current-Voltage (I-V) Characterization

The I-V characterization is an extensively employed and significant technique for evaluating the efficiency of a hybrid photodetector. Figure 2.11illustrates the setup for measuring the photocurrent.

The electrical properties of the photodetectors are evaluated using a Keithley 2612 sourcemeter. Current is measured while sweeping the voltage bias from -1 V to 1 V for ZnO/P3HT devices. The measurements are conducted in the dark initially and then under a monochromatic light source. The characterization systems used for semiconductor films and devices are depicted in Figure2.11. The figures of merit for photodetectors encompass various important performance parameters, which are summarized below :

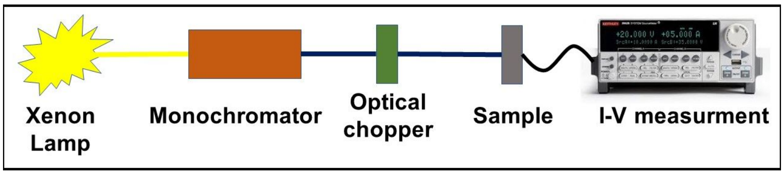


Fig. 2.11: **Photo current measurement setup**

1. **Spectral Response Range:** The spectral response range of a photodetector refers to the specific range of wavelengths over which it operates effectively. This is because photons with energies equal to or greater than the bandgap energy are capable of generating electron-hole pairs in the material. Consequently, beyond a certain wavelength, the light will not be absorbed by the material, as the energy of a photon is inversely proportional to its wavelength. Thus, each semiconductor material has a limited range of wavelengths in which it can be utilized. The upper wavelength limit λ_c is determined by the bandgap energy E_g of the material, and can be calculated using the equation:

$$\lambda_c = \frac{hc}{E_g} \tag{2.13}$$

   When designing a photodetector, the crucial consideration is to select a suitable material that can effectively respond to the desired photo signal. In the context of this thesis, the focus is on visible, ultraviolet, and near-infrared (NIR) photodetectors.

2. **Photocurrent (I_{ph}):** The presence of an electric field within the device facilitates the movement of photo-generated charge carriers towards the corresponding charge collecting electrodes. As a result, a current is established within the external circuit. This current, known as the photocurrent I_{ph} , is a direct consequence of the swept charge carriers caused by the electric field.

3. **Rectification Ratio:** The rectification ratio (RR) is a significant performance indicator for photodetectors. It provides insights into the rectification behavior of the device. The RR is defined as the ratio between the forward bias or On-current I_{ON} and the reverse bias or Off-current I_{OFF}at a specified voltage (+2V and -2V). The rectification ratio (RR) can be calculated using the following equation:

$$\text{Rectification Ratio} = \frac{I_{\text{ON}}}{I_{\text{OFF}}} \tag{2.14}$$

   By evaluating the rectification ratio, we can assess the efficiency of the photodetector in converting current under forward and reverse biases. A higher rectification ratio indicates a stronger rectification capability and better performance of the photodetector.

4. **Detector Responsivity (R):** Detector Responsivity refers to the efficiency of a device in detecting different wavelengths, and it is defined as the ratio of the output current signal to the optical power of the input signal. It is a measure of how effectively the device converts optical power into electrical current. The equation for detector responsivity is given by as:

$$R = \frac{I_{\text{ph}}}{P_{\text{o}}} \tag{2.15}$$

   where I_{ph} represents the photo-induced current and P_O represents the incident optical power from the optical source. The unit of responsivity is $[\mathrm{A\,W^{-1}}]$. The spectral response of a photodetector, which shows how its responsivity varies with wavelength, is often considered when selecting a detector for a specific application in a particular wavelength range.

5. **Photosensitivity (S):** Photosensitivity (S) is a measure of the device's ability to generate photocurrent compared to its dark current. It is defined as the ratio of the photocurrent I_{ph} to the dark current I_{dark} of the device. The equation for photosensitivity is given as:

$$S = \frac{I_{\text{ph}}}{I_{\text{dark}}} \tag{2.16}$$

   This parameter quantifies the sensitivity of the device to incident light, with higher values indicating a stronger response to light compared to the background dark current.

6. **Reverse Saturation Current:** The reverse saturation current I_O refers to a small current that is produced within the circuit when a photodiode is subjected to a small reverse voltage while being reverse biased. This current arises as a result of the flow of charge carriers in the opposite direction to the applied voltage.

7. **External Quantum Efficiency (EQE):** External Quantum Efficiency (EQE) refers to the ratio of the number of electron-hole pairs generated by incident photons to the total number of photons incident on the photo-detector. It represents the efficiency of converting photons into an output current. Not all generated electron-hole pairs contribute to the photocurrent since some of them recombine within traps. Therefore, the quantum efficiency reflects the probability that a single incident photon will generate an electron-hole pair that contributes to the photo-detector's output current. The external quantum efficiency depends on factors such as the number of photons irradiated onto the semiconductor, the number of photons absorbed and converted to carriers, and the number of carriers that reach the external circuit before recombination occurs. It can be calculated using the equation:

$$\eta = \frac{I_{\text{ph}}/q}{P_{\text{o}}/h\nu}, \quad 0 < \eta < 1 \tag{2.17}$$

   Here, P_O represents the optical power of the incident light source in watts. The absorption of the semiconducting material is wavelength-dependent, which means that the external quantum efficiency of the photo-detector also varies with wavelength. However, EQE remains independent of the energy of the incident photons.

8. **Response Time:** Response Time is an important characteristic of a photo-detector as it determines the device's ability to quickly track changes in the input optical signal. It quantifies the speed at which the detector can respond to variations in the intensity of the incident light. The measurement of response time involves sending light pulses to the photo-detector and observing how rapidly it can react to these signals.

9. **Specific detectivity (D*):** Specific detectivity is a key parameter used to evaluate the performance of photodetectors. It measures the ability of a detector to detect weak optical signals while considering various noise sources. D* takes into account factors such as the responsivity of the detector, the noise equivalent power (NEP), and the detector's active area. Specific detectivity is calculated using the formula:

   $$D^* = R \times \sqrt{\frac{A}{2eI_d}} \tag{2.18}$$

   Where R is responsivity and A_o is the area of the photodetector, e represents the charge of an electron, and I_d is the dark current.

   A higher value of D* indicates better sensitivity and performance of the photodetector, as it signifies a higher signal-to-noise ratio. A high D* allows for the detection of weaker optical signals with greater accuracy and reliability.

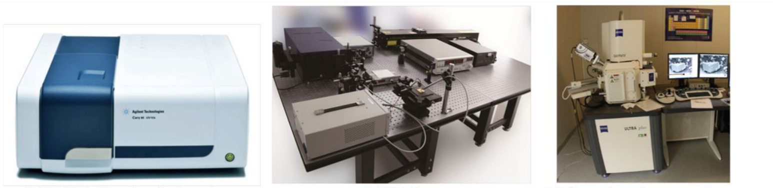
(a) Spin Coater

(b) Annealing Oven

(c) Glove Box

(d) PVD System

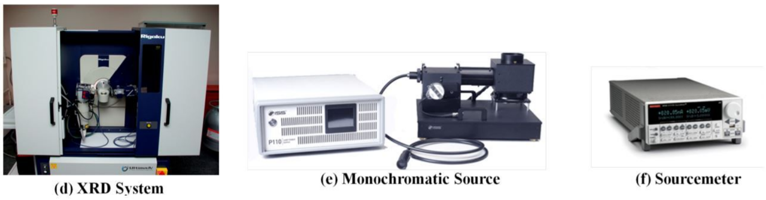
Fig. 2.12: **: Instruments used for the fabrication of devices**



(a) UV-Vis Spectrophotometer

(b) PL System

(c) Scanning electron microscopy



(d) XRD System

(e) Monochromatic Source

(f) Sourcemeter

Fig. 2.13: **Instruments used for characterization of devices**

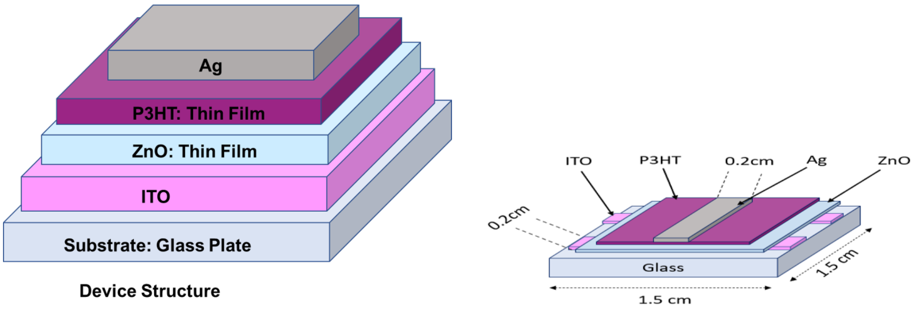
Chapter 3

The Fabrication of ZnO/P3HT Hybrid Photodetector

This chapter explores the utilization of the ZnO/P3HT inorganic-organic hybrid material in photodetectors. This material combines the distinctive properties of zinc oxide (ZnO) and poly(3-hexylthiophene) (P3HT) to achieve efficient light detection. ZnO serves as the electron-transporting layer, providing excellent charge mobility and conductivity. It establishes the foundation for effective charge separation and collection. Conversely, P3HT acts as the light-absorbing layer, facilitating efficient absorption of photons. The fabrication process entails depositing ZnO and P3HT layers, resulting in a heterojunction formation. This heterojunction enables the efficient separation of photogenerated charges. The ZnO/P3HT hybrid structure offers several advantages. It combines the superior electron mobility and conductivity of ZnO with the light absorption capabilities of P3HT, leading to enhanced photoresponse. The heterojunction interface facilitates efficient charge separation and collection, thereby improving the overall performance of the device. In conclusion, ZnO/P3HT inorganic-organic photodetectors hold immense promise for light sensing applications, leveraging the synergistic integration of inorganic and organic materials.

3.1 Introduction

Photodetectors based on pi-conjugated polymers hold great potential for future low-cost applications, particularly in printable form, enabling large-area photodetector arrays and scanners. The efficiency of organic photodetectors depends on photon absorption, exciton dissociation, and charge collection. Bulk heterojunction photodetectors with mixed donor and acceptor phases address the issue of charge trapping and recombination loss, enhancing overall performance. To further improve low-cost optoelectronic devices, the substitution of organic n-type materials with inorganic counterparts is beneficial, combining the advantages of both materials[67][68]. The primary objective of his research is centered around the creation of photodetectors that combine organic and inorganic components. This involves utilizing RR-P3HT, an organic material with p-type characteristics, and ZnO, an inorganic material with n-type properties. ZnO possesses a wide band gap and a substantial exciton binding energy, making it highly adaptable for implementing nanostructures in various device applications[69][70]. By constructing well-organized hybrid bulk heterojunction structures, excitons are generated within the conjugated polymer and subsequently dissociate at the interfaces between ZnO and the conjugated polymer[71]. The resulting separated charge carriers then travel through their respective materials and are eventually collected by the outer electrodes[72].



((a)) **Device Structure** *((b))* **Decvice Schematic**

Fig. 3.1: **Device structure and schematic details**

3.2 Experimental Details

1. **Experiment Details** To fabricate the device , commercially available Indium tin oxide (ITO)-coated glass substrates with a resistivity of $10\,\Omega/\text{cm}^2$ were first patterned and then underwent a sequential cleaning process involving ultrasonication in a soap solution, followed by rinsing with acetone, isopropanol, and distilled water. The ZnO seed layers were prepared using a colloidal solution consisting of anhydrous zinc acetate $(Zn(CH_3COOH)_2)$ and ethanolamine as a precursor dissolved in 2-methoxyethanol. Ethanolamine was added to improve the solubility of zinc acetate in

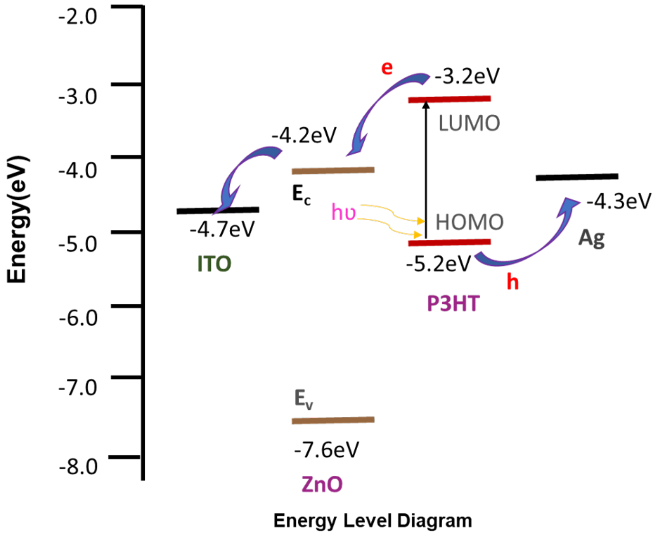


Fig. 3.2: **Energy diagram of device structure**

2-methoxyethanol. The solution was stirred at 60°C for 6 hours and then spin coated onto the patterned ITO-coated glass substrate at a speed of 3000 rpm for 30 seconds(Acceleration for 10 seconds and Deceleration for 20 seconds). Subsequently, the substrates were annealed in air at 240°C for 5 minutes to enhance the adhesion of the ZnO particles to the substrate. The thickness of the pristine ZnO layer (1M seed solutuion single layer coating over Glass Substrate) was determined to be 390 nm using cross-sectional FESEM imaging[73][74].

For the experiment, RR-P3HT was employed as the donor and the active material responsible for light absorption. The P3HT used was obtained from Sigma Aldrich with a molecular weight (Mw) of 70,000 kDa and regioregular structure. No additional modifications were made to the P3HT. To prepare a thin film, a 2wt% solution of P3HT was created in Chloro-Benzene, which was then subjected to spin coating at 800 rpm for 40 seconds(Acceleration for 10 seconds and Deceleration for 30 seconds). Afterward, the film underwent annealing in a vacuum at 135°C for 22 minutes[75].

Lastly, a top electrode made of Ag was thermally deposited using a physical vapor deposition system at a pressure of 2×10^{-6} mbar

The UV-visible spectral measurements were conducted using an Agilent Technologies Cary 60 UV-Vis spectrophotometer, covering a wavelength range of 200 nm to 800 nm. Prior to each absorption spectra measurement, the ITO-coated glass substrate was utilized for baseline correction. All characterizations took place under ambient conditions. A monochromatic light emitted by an ISS P110 monochromator with a wavelength range of 200 nm to 800 nm, originating from a Xenon lamp, was directed onto the bottom surface of the ITO substrates of the hybrid photodetector[76]. To ensure equal illumination area as the active electrode of the photodetector, a photomask was employed. The active device area was measured to be 0.04 cm^2 . The intensity of the incident light on the device was set to $1\,\mathrm{mW/cm}^2$ by attenuating the light beam using a neutral density filter. The Current-Voltage (I-V) characteristics of the photovoltaic devices were measured using a Keithley 2612 A Dual Channel SourceMeter Unit. Subsequently, the obtained results were analyzed and compared during the study of the outcomes[77].

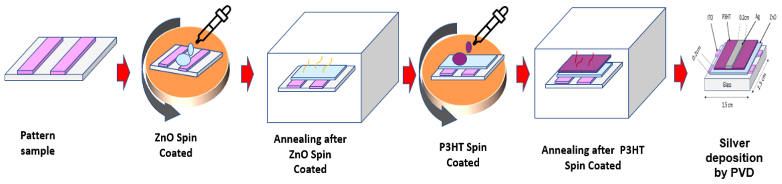


Fig. 3.3: **Schematic of fabrication process**

3.3 Results and Discussion

3.3.1 Absorption Spectroscopy Study

1. **RR-P3HT Films:**

   The morphological structure of spin-coated rr-P3HT films is predominantly amorphous, characterized by coiled and staggered polymer chains. This structural characteristic is reflected in the absorption spectra of the films. Figure 3.4

   The absorption spectra of the spin-coated polymer films were analyzed, revealing a slight blue-shift in the absorption spectrum of the spin-coated P3HT film. This shift was accompanied by less prominent vibronic shoulders. The blue-shifted λmax can be attributed to a decrease in the effective length of π-conjugation, which is caused by

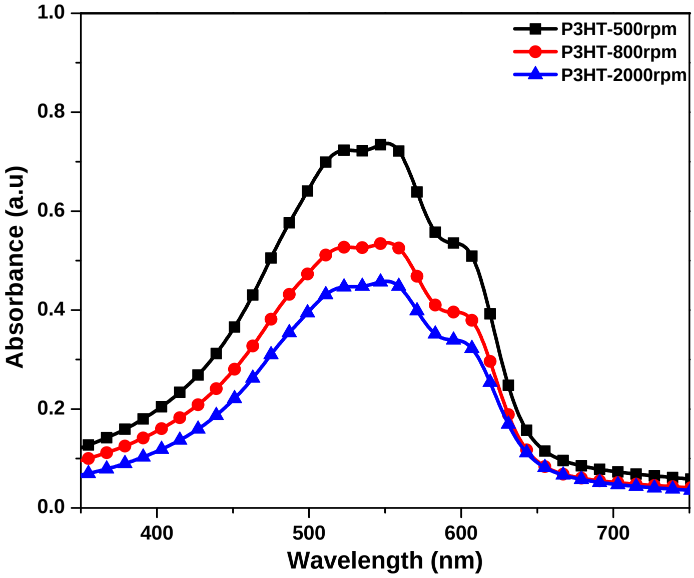


Fig. 3.4: **Absorbance Spectra of P3HT thin films**

non-oriented fractions of the polymer chains. The vibronic shoulders observed at 520 nm and 620 nm correspond to the 0-1 and 0-0 π-π* electronic transitions, respectively[53][55].

The absorption spectrum of the rr-P3HT thin film can be explained by a model consisting of two components. The lower energy part of the spectrum corresponds to the crystalline regions of the film, which contribute to the formation of weakly interacting H-Aggregate states. The higher energy part originates from the amorphous regions of the film, which consist of disordered chains. The ratio between the 0-0 and 0-1 vibronic bands can be used to determine the free exciton bandwidth (W) of these aggregates. A smaller value of W indicates a greater extent of effective π-conjugation along the polymer backbone[57]. These parameters are interconnected by the following equation:

$$\frac{A_{0\text{-}0}}{A_{0\text{-}1}} \approx \left(\frac{1-0.24W/Ep}{1+0.073W/Ep}\right)^2 \tag{3.1}$$

Here, the symbol $'W'$ denotes the effective length of π-conjugation, while $'E_p'$ denotes the energy related to the intramolecular vibrations of the polymer[58].

2. **ZnO Thin Films:**

Absorption spectroscopy was conducted to examine the absorption spectrum of the ZnO samples. These samples were prepared by spin coating of different molarity seed solutions onto cleaned hydrophilic glass samples.

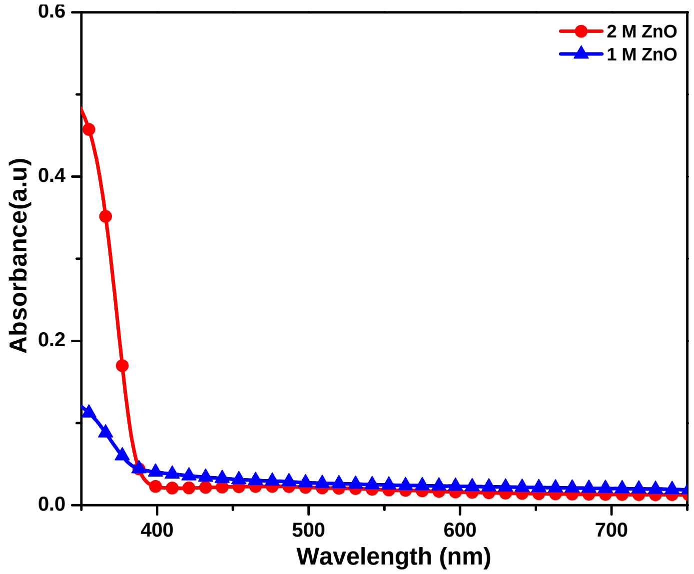


Fig. 3.5: **Absorbance Spectra of ZnO thin films**

Samples made with 1M and 2M seed solution. A cleaned glass sample was used as a reference during the absorption spectroscopy study.

As depicted in the figure 3.5, the pristine ZnO sample exhibited significant near-band UV absorption, which corresponds to the band edge absorption of ZnO. Notably, the absorption peak increased as the molarity of the spin-coated ZnO seed solution was increased[44][49].

3. **ZnO-P3HT Thin Films:**

Absorption spectroscopy was performed to analyze the absorption spectrum of the ZnO-P3HT thin film-coated samples.

These samples were prepared by initially spin coating a ZnO thin film onto a cleaned hydrophilic processed glass substrate, followed by spin coating a P3HT thin film onto the ZnO-coated samples. A cleaned glass sample was used as a reference during the absorption spectroscopy study. As shown in Figure 3.6, the pristine ZnO sample displayed noticeable absorption in the near-band UV region, indicating band edge absorption of ZnO. The P3HT thin film exhibited significant absorption in the visible range, specifically around 500nm to 620nm[48][57].

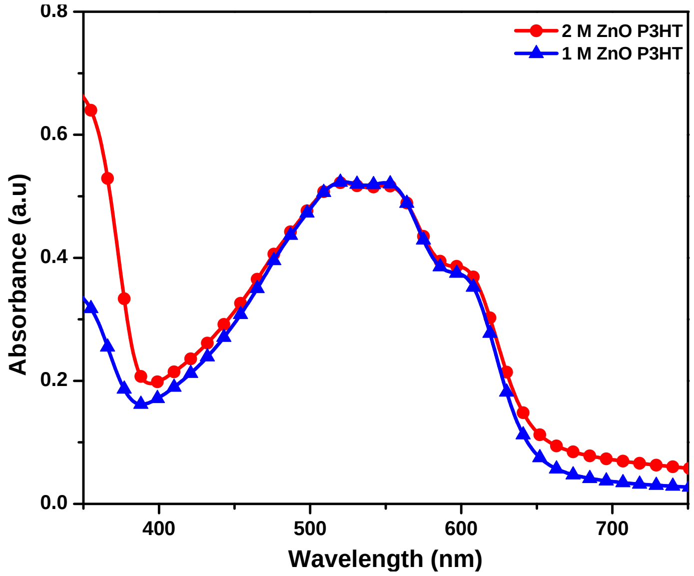
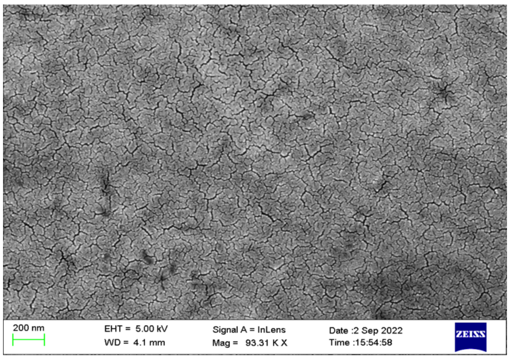


Fig. 3.6: **Absorbance Spectra of ZnO-P3HT thin films**



Top view of spin-coated P3HT thin film

Fig. 3.7: **FESEM image of P3HT thin film**

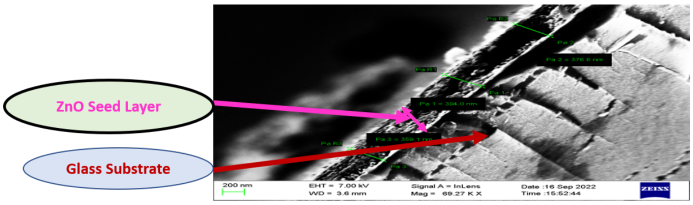
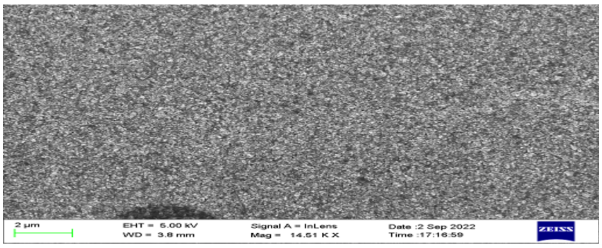


Fig. 3.8: **FESEM image of cross section of ZnO thin film**



Top view of spin-coated ZnO seed layer thin film

Fig. 3.9: **FESEM image of ZnO thin film**

3.3.2 Field Emission Scanning Electron Microscopy Study

Field Emission Scanning Electron Microscopy (FESEM) analysis was conducted to examine the morphology of spin-coated thin films of P3HT and ZnO, as well as to measure the thickness of the ZnO thin film.

3.3.3 Electrical Characterization of ZnO/P3HT Device

The performance of a photodetector is evaluated through current-voltage (I-V) curves, which provide key parameters related to its performance. The hybrid ITO/ZnO/P3HT/Ag photodetector schematic is shown in Figure 3.1.

It is noteworthy to mention that in the absence of light, the photodetector exhibits similar characteristics to a standard rectifying junction diode. When a forward bias is applied, there is a significant flow of current above the built-in voltage, displaying an exponential growth. On the other hand, when a reverse bias is applied, only a relatively small current passes through the diode . The response of the photodiode when exposed to light can be described using the Schottky equation, which is typically used to analyze the behavior of rectifying diodes, as shown in equation (1.1).

$$I = I_{\text{sat}} \left(e^{\frac{V}{\eta V_t}} - 1 \right)$$

where I is the diode current, I_{sat} is the reverse saturation current, V is the applied voltage, η is the ideality factor, and V_t is the thermal voltage (26 mV).

When incident light illuminates the photo diode, the current-voltage curve shifts by an amount I_{ph}, given by:

$$I_{\text{total}} = I_{\text{sat}} \left(e^{\frac{V}{\eta V_t}} - 1 \right) + I_{\text{ph}} \tag{3.2}$$

where I_{ph} is the photo current, which depends on the intensity of the incident light.[21][29]

Dark current, also referred to as diode current, is the current generated when the photodetector is not exposed to any illumination.

The ITO/ZnO/P3HT/Ag hybrid photodetector was fabricated, and its photo response performance was studied for different wavelengths. Figure 3.10 shows the logarithmic current-voltage (I-V) characteristics of the ITO/ZnO/P3HT/Ag photodetector under both dark conditions and illumination at various wavelengths[30].

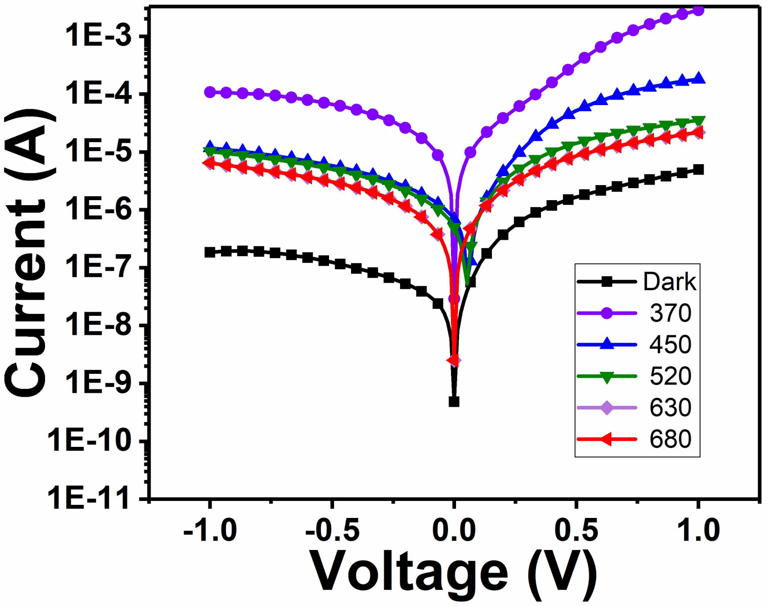


Fig. 3.10: **I-V characteristics of ITO/ZnO/P3HT/Ag device**

The dark current is minimum due to a large charge injection barrier under reverse bias. Under dark conditions, the reverse saturation current measured at -1 V is 1.83 $\times 10^{-7}$ A, and the forward current of the photo diode measured at 1 V is 5 $\times 10^{-6}$ A, resulting in a rectification ratio of **27.32**.

Using an I-V setup, we measured the photo response at different wavelengths by illuminating the photodetector. After obtaining the photo response at various wavelengths, we analyzed the I-V results and calculated parameters such as photo sensitivity, responsivity, specific detectivity, and external quantum efficiency (EQE) for wavelengths of 370 nm, 450 nm, 520 nm, 630 nm, and 680 nm, as presented in the table 3.1.

Photovoltaic Effect

The photovoltaic effect in a hybrid photodetector refers to the phenomenon where incident light is converted into electrical energy. It occurs when photons from the incident light interact with the active material in the photodetector, causing the generation of electron-hole pairs. These photo-generated charge carriers are then separated and collected by the built-in electric field within the photodetector. This process leads to the generation of

	370 (nm)	**450 (nm)**	**520 (nm)**	**630 (nm)**	**680 (nm)**
$I_{ph}(\lambda)$ **(A)**	1.17×10^{-5}	1.17×10^{-5}	1.02×10^{-5}	6.45×10^{-6}	6.45×10^{-6}
$S(\lambda)$	584.67	62.93	54.74	34.25	34.25
$R(\lambda)$ [A W^{-1}]	2.4075	0.2879	0.2504	0.1566	0.1566
D* (Jones)	1.98×10^{12}	0.24×10^{12}	0.206×10^{12}	0.13×10^{12}	0.13×10^{12}
EQE (%)	80.68	79.33	59.71	30.82	28.55

Table 3.1: **I-V parameters of ITO/ZnO/P3HT/Ag device**

a voltage or electric current, which can be measured and utilized for various applications[36].

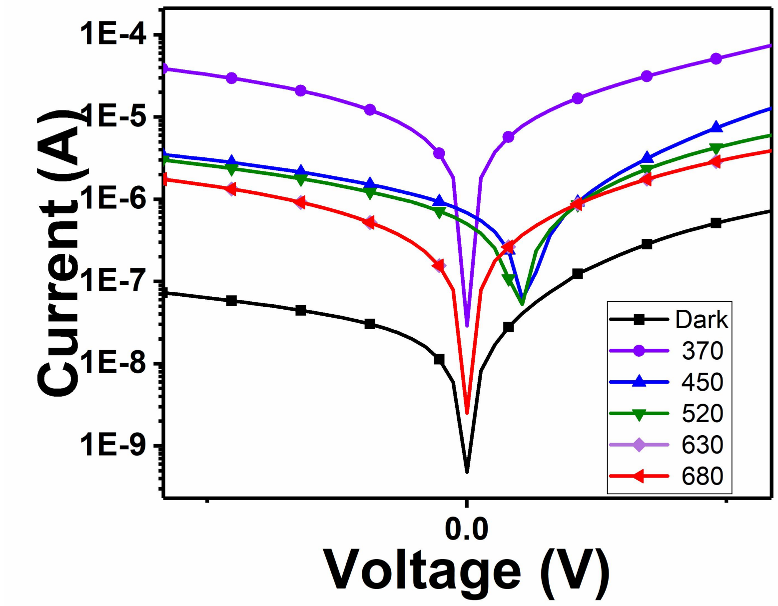


Fig. 3.11: **Photovoltaic effect study of ITO/ZnO/P3HT/Ag device**

In a hybrid photodetector, the photovoltaic effect plays a crucial role in converting light energy into an electrical signal. By optimizing the design and materials of the photodetector, the efficiency of the photovoltaic effect can be enhanced, resulting in improved sensitivity, responsivity, and overall performance of the device. The photovoltaic effect is a fundamental principle underlying the operation of hybrid photodetectors and is instrumental in their ability to detect and convert light into useful electrical signals[37].

While analyzing the I-V data of the ITO/ZnO/P3HT/Ag hybrid photodetector, we observed a photovoltaic effect at wavelengths of 450 nm and 520 nm as shown in Figure 3.11 . It was observed that the device exhibits a dark current of 4.8 $\times 10^{-10}$ A at zero bias.

	450 (nm)	**520 (nm)**
$I_{ph}(\lambda)$ **(A)**	4.4×10^{-7}	6.7×10^{-7}
$S(\lambda)$	1400	916.7
$R(\lambda)$ [A W^{-1}]	0.017	0.011
D* (Jones)	2.7×10^{11}	1.7×10^{11}
EQE(%)	4.68	2.62

Table 3.2: **Zero bias I-V parameters of ITO/ZnO/P3HT/Ag device**

We further analyzed the I-V results and calculated additional parameters, including photo sensitivity, responsivity, specific detectivity, and external quantum efficiency (EQE), for the wavelengths of 450 nm and 520 nm. The results of these calculations are presented in the table 3.2 .

3.4 Summary

The research primarily focuses on fabricating and studying hybrid photodetectors using ZnO/P3HT materials. This combination merges the light absorption abilities of P3HT with the electron-transporting properties of ZnO, leading to enhanced photo response for photo detection purposes. The fabrication process involves depositing layers of ZnO and P3HT to form a heterojunction, where the ZnO layer acts as an electron-transporting layer with excellent charge mobility and conductivity.

The specific goal of the research is to develop ZnO/P3HT hybrid photodetectors capable of detecting near-ultraviolet (UV) light at 370 nm and visible light at 520 nm. These photodetectors exhibit high sensitivity to light. Additionally, the study focuses on utilizing cost-effective solution processing techniques to manufacture ZnO/P3HT hybrid photodetectors. The aim is to improve various performance parameters of the photodetectors in the UV-Vis range, including achieving the desired rectification ratio and sensitivity to light.

During the analysis of the results, the researchers also observed a photovoltaic effect at wavelengths of 450 nm and 520 nm.

Overall, the research strives to advance the fabrication techniques and performance of ZnO/P3HT hybrid photodetectors by combining the unique properties of inorganic and organic materials. By optimizing the fabrication process and enhancing various performance parameters, these photodetectors have the potential to be used in a wide range of applications that require efficient and cost-effective photo detection capabilities

Chapter 4

Development of Hybrid NIR Photodetector

We conducted an investigation on the performance of organic photodetectors by utilizing a bulk heterojunction of P3HT and Squaraine dye blends. Our main objective was to develop a near-infrared (NIR) hybrid photodetector that has potential applications in the medical field. To achieve this, we blended the Squaraine dye with P3HT, which has absorption properties in the NIR range.

In our study, we specifically focused on examining the impact of blending Squaraine dye with P3HT on the performance of the hybrid photodetector (ITO/ZnO/P3HT-DYE Blend/Ag). These photodetectors were created by combining two different materials in the bulk heterojunction structure, and they were designed to respond to specific wavelengths that corresponded to the maximum absorption of each respective material.

4.1 Introduction

Organic opto electronic devices have gained significance due to their lightweight, cost-effective, and flexible nature, surpassing traditional inorganic photodetectors. Research on organic photodetectors has increased, driven by applications in radiation detection, medical advancements, military uses, and space research.For high-performance devices, organic photodetectors require a strong light-absorbing active layer, high charge carrier mobility, and appropriate energy level alignment[78].

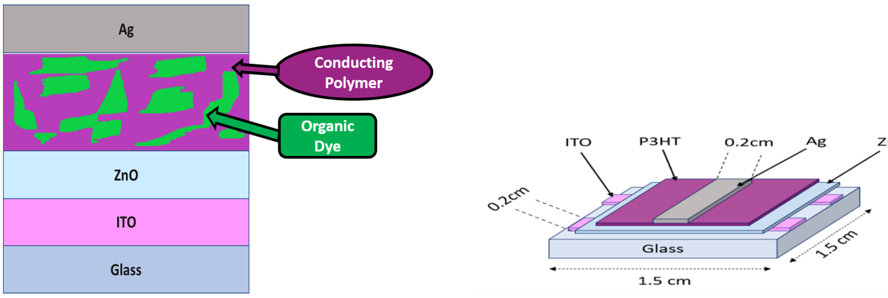
Organic semiconductors are divided into conjugated polymers and small molecules, each offering unique advantages for efficient device fabrication.Small molecule-based devices face solubility challenges in solution processing, often requiring expensive thermal evaporation processes that limit device coverage.Small molecule films exhibit better uniformity and well-defined structures, improving optoelectronic properties compared to conjugated polymers[79][80].

Blending organic materials enhances device properties by combining advantageous characteristics. Blending small molecules with polymeric semiconductors improves solution processability and enhances device performance.Extensive research has focused on regio-regular poly(3-hexylthiophene) (rrP3HT) and the blend of poly(3-hexylthiophene) (P3HT) with phenyl-C61-butyric acid methyl ester (PC61BM) for their promising optoelectronic properties.Blending inexpensive donor-only species, such as Pentacene, Alq3, oligothiophenes, and para-hexaphenyl (PHP), can improve the performance of optoelectronic devices[74][76].

In our study, we synergistically combined the rr-P3HT polymer with Squaraine dye to leverage the distinctive properties exhibited by both materials. Our primary aim was to develop a near-infrared (NIR) hybrid photodetector, for which we selected the Squaraine dye due to its excellent absorption characteristics in the NIR range. [81][82]Both the polymer and Squaraine dye can be dissolved in common organic solvents, with the Squaraine dye exhibiting high solubility in chlorobenzene and P3HT demonstrating good solubility as well[63][65]. Consequently, we utilized chlorobenzene as the solvent in our investigation to dissolve both P3HT and Squaraine dye.

We fabricated a PN junction photodiode structure on an ITO-coated glass substrate using the blend systems. The transparency of ITO allows light to reach the active layer of the device. Subsequently, we measured both the dark current and photocurrent of the fabricated devices using an I-V measurement system[83].

Blending the Squaraine dye with P3HT resulted in significant improvements in photoresponse and wavelength tunability of the fabricated devices. To determine the tunable range of wavelengths for optimal photoresponse, we conducted absorption spectroscopy studies[84][85]. After obtaining the wavelength data for the individual materials and the blend, we proceeded with device fabrication and performed electrical characterization on all the fabricated devices. The collected data were thoroughly analyzed to complete our analysis[86][87].



((a)) **Device Structure** *((b))* **Decvice Schematic**

Fig. 4.1: **Device structure and schematic of ITO/ZnO/P3HT:DYE Blend/Ag device**

4.2 Experimental Details

Prior to use, commercially available Indium tin oxide (ITO)-coated glass substrates with a resistivity of $10\,\Omega/\mathrm{cm}^2$ underwent a sequential cleaning process. This involved ultrasonication in a soap solution, followed by rinsing with acetone, isopropanol, and distilled water[29].

Next, a ZnO seed layer was applied to the ITO-coated glass substrate. The seed layers were prepared by utilizing a colloidal solution consisting of anhydrous zinc acetate $[Zn(CH_3COOH)_2]$ and ethanolamine as a precursor dissolved in 2-methoxyethanol. Ethanolamine was added to enhance the solubility of zinc acetate in 2-methoxyethanol. The solution was stirred at 60°C for 1 hour and then spin coated onto the patterned ITO-coated glass substrate at a rate of 3000 rpm for 30 seconds. Subsequently, the substrates were annealed in air at 240°C for 5 minutes to improve the adherence of ZnO particles to the substrate[74]

The active materials employed in this study included RR-P3HT as the donor and light-absorbing material, and Squaraine dye as the acceptor and light-absorbing small molecule material. The P3HT utilized was sourced from Sigma Aldrich with a molecular weight of 70,000 kDa, and no further modifications were made to it. To coat a thin film of blend of P3HT and Squaraine dye , a solution with a 2 wt% was prepared using chlorobenzene solvent. This solution was subsequently used for spin coating. The ratio of Squaraine dye to P3HT in the blend was **1:5**, allowing for the preparation of the desired 2 wt% weight solution[88].

The spin coating process was conducted at 800 rpm for 40 seconds. The resulting film was then annealed at 135°C for 22 minutes. To complete the fabrication of the photodetector, **Ag** was thermally deposited as the top electrode using a physical vapor deposition system under a pressure of 2×10^{-6} mbar. The schematic of the photodetector fabrication can be seen in the figure.

The UV-visible spectral measurements were conducted using an Agilent Technologies Cary 60 UV-Vis spectrophotometer, which covered a wavelength range of 200 nm to 800 nm. Prior to each absorption spectrum measurement, the ITO coated glass substrate was utilized for baseline correction, ensuring accurate reference correction.

All characterizations took place under ambient conditions.A monochromatic light emitted by an ISS P110 monochro-mator with a wavelength range of 200 nm to 800 nm, originat-ing from a Xenon lamp, was directed onto the bottom sur-face of the ITO substrates of the hybrid photodetector. To ensure equal illumination area as that of the active electrode area of the photodetector, a photomask was employed. The active device area measured 0.04 cm^2. The intensity of the incident light was adjusted to the desired level by employing a neutral density filter. The intensity of the incident light on the device was set at $1\,mW/cm^2$. The Current-Voltage (I-V) characteristics of the photovoltaic devices were measured using a Keithley 2612 A Dual Channel SourceMeter Unit[33][84][89][90].

4.3 Results and Discussion

4.3.1 Absorption Spectroscopy Study

1. **Squarine Dye Thin Film:**

   The morphological structure of spin-coated Squarine dye films is predominantly amorphous.These samples were prepared by spin coating Squarine dye solution onto cleaned hydrophobic glass samples.Solution prepared in two solvents .one is clorobenzene and another is chloroform[64].

   first by taking 2 mg squarine dye into 1 ml clorobenzene solvent and another by taking 2 mg squarine dye into 1 ml chloroform solvent . This structural characteristic is reflected in the absorption spectra of the films. Figure 4.2 illustrates the absorption spectra of the spin-coated pristine Squarine dye thin films. The Squaraine dye exhibits significant absorption in the wavelength range of 600 nm to 750 nm, characterized by two prominent peaks at 634 nm and 680 nm[65].

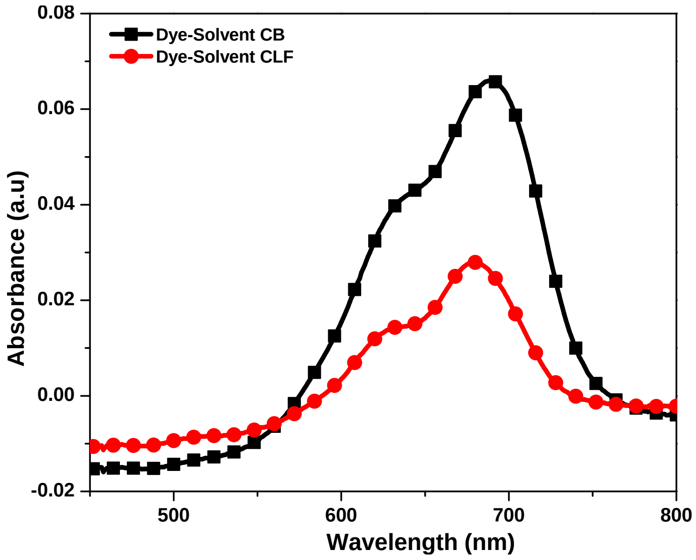


Fig. 4.2: **Absorbance Spectra of Squarine dye thin film**

2. **Squarine Dye-P3HT Blend Thin Film:**

   Absorption spectroscopy was conducted to examine the absorption spectrum of the thin films of blend of P3HT and Squarine dye samples. These samples were prepared by spin coating of blend solution of of P3HT and Squarine dye onto cleaned hydrophobic glass samples[60][55].

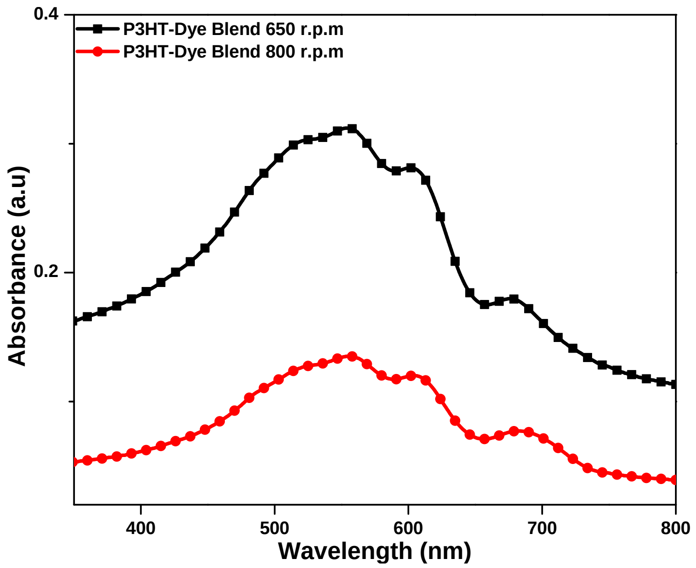


Fig. 4.3: **Absorbance Spectra of Squarine dye-P3HT blend thin film**

The active materials employed in this study included RR-P3HT as the donor and light-absorbing material, and Squaraine dye as the acceptor and light-absorbing small molecule material. The P3HT utilized was sourced from Sigma Aldrich with a molecular weight of 70,000 kDa, and no further modifications were made to it. To create a thin film, a solution with a 2wt% ratio blend of P3HT and Squaraine dye was prepared using chlorobenzene solvent. This solution was subsequently used for spin coating. The ratio of Squaraine dye to P3HT in the blend was **1:5**, allowing for the preparation of the desired 2wt% weight solution[57][66].

Figure 4.3 illustrates the absorption spectra of the spin-coated pristine Squarine dye thin films.

4.3.2 Electrical Characterization of ZnO/P3HT Device

The performance of a photodetector is evaluated through current-voltage (I-V) curves, which provide key parameters related to its performance. The **ITO/ZnO/P3HT:Squarine dye blend/Ag** hybrid photodetector schematic is shown in Figure 4.1. It is important to note that under dark conditions, the characteristics of the photodetector resemble those of a conventional rectifying junction diode. Under forward bias, large currents flow above the built-in voltage, exhibiting an exponential increase. Conversely, under reverse bias, a relatively small current flows through the diode. The dark current, also known as the diode current, refers to the current generated when the photodetector is not illuminated[31][32].

The behavior of the photodiode under illumination can be described by the Schottky equation for a rectifying diode, as shown in equation (1.1).

$$I = I_{\text{sat}}\left(e^{\frac{V}{\eta V_t}} - 1\right)$$

where I is the diode current, I_{sat} is the reverse saturation current, V is the applied voltage, η is the ideality factor, and V_t is the thermal voltage (26 mV).

When incident light strikes the photo diode, the curve shifts by the quantity I_{ph}, representing the photo current, which depends on the intensity of the incident light as given by equation (3.2).

$$I_{\text{total}} = I_{\text{sat}}\left(e^{\frac{V}{\eta V_t}} - 1\right) + I_{\text{ph}}$$

where I_{ph} is the photo current, which depends on the intensity of the incident light

The impact of incorporation of Squarine dye on the per-

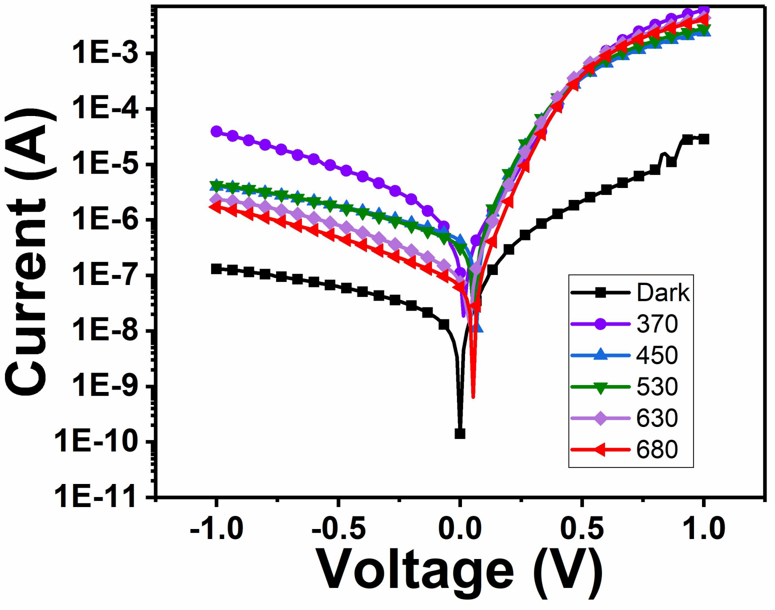


Fig. 4.4: **I-V characteristics of ITO/ZnO/P3HT:Dye Blend/Ag device**

formance of the **ITO/ZnO/P3HT:Squarine dye blend/Ag** hybrid photodetector has been studied. Figure 4.4 shows the logarithmic I-V characteristics of the **ITO/ZnO/P3HT:Squarine dye blend/Ag** hybrid photodetector under dark conditions and under light illumination at different wavelengths[88] .

	370 (nm)	**450 (nm)**	**520 (nm)**	**630 (nm)**	**680 (nm)**
$I_{ph}(\lambda)$ **(A)**	3.4×10^{-5}	4.01×10^{-6}	4.3×10^{-6}	2.30×10^{-6}	1.71×10^{-6}
$S(\lambda)$	260.54	29.85	32.08	16.77	12.15
$R(\lambda)$ $[\mathrm{A\,W^{-1}}]$	0.8475	0.097	0.104	0.054	0.04
D* (Jones)	1.02×10^{12}	0.116×10^{12}	0.124×10^{12}	0.065×10^{12}	0.048×10^{12}
EQE (%)	281.51	26.72	24.33	10.62	7.29

Table 4.1: **I-V parameters of ITO/ZnO/P3HT:Squaraine dye/Ag device**

The dark current is minimum due to a large charge injection barrier under reverse bias. Under dark conditions, the reverse saturation current measured at -1 V is 1.3 $\times 10^{-7}$ A, and the forward current of the photo diode measured at 1 V is 2.84 $\times 10^{-5}$ A, resulting in a rectification ratio of **218.46**. Using an I-V setup, we measured the photo response at different wavelengths by illuminating the photodetector. After obtaining the photo response at various wavelengths, we analyzed the I-V results and calculated parameters such as photo sensitivity, responsivity, specific detectivity, and external quantum efficiency (EQE) for wavelengths of 370 nm, 450 nm, 520 nm, 630 nm, and 680 nm, as presented in the table 4.1.

Photovoltaic Effect

The photovoltaic effect is a fundamental process that converts light energy into electrical energy. It serves as the foundation for various photodetector technologies, including hybrid photodetectors that utilize different materials, such as inorganic and organic semiconductors. This combination enables the exploitation of unique properties and improves the overall performance of the devices. [36].

In a hybrid photodetector, the photovoltaic effect occurs when incident photons with sufficient energy strike the active region of the device. These photons transfer their energy to the semiconducting materials, generating electron-hole pairs. The inorganic semiconductor component, often made of materials like silicon or metal oxides, provides efficient charge transport and collection. Meanwhile, the organic semiconductor component, typically based on conjugated polymers or small molecules, offers tunable absorption properties and flexibility.

The generated electron-hole pairs in the hybrid photodetector create a built-in electric field, leading to charge separation. The electrons migrate towards the electrode with a lower potential, while the holes move towards the electrode with a higher potential. This charge separation creates a voltage difference, known as the photovoltage, across the device[37].

By connecting external electrodes to the hybrid photodetector, the photogenerated current can be extracted and measured. This current, known as the photocurrent, is directly proportional to the intensity of incident light and can be used for various applications, such as light sensing, imaging, and energy conversion.

The hybrid nature of these photodetectors allows for a broader spectral response range, high sensitivity, and tunable properties. The combination of inorganic and organic semiconductors enables efficient light absorption across a wide range of wavelengths, including the visible and near-infrared regions. Ad-

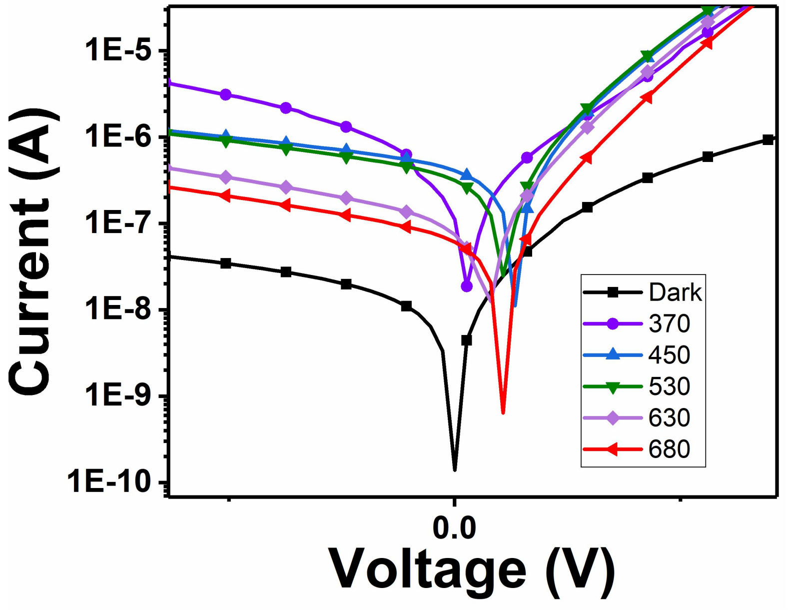


Fig. 4.5: **Photovoltaic effect study of ITO/ZnO/P3HT:Dye Blend/Ag device**

ditionally, the flexibility and processability of organic materials offer the potential for low-cost and large-area device fabrication.

In summary, the photovoltaic effect plays a crucial role in hybrid photodetectors, enabling the conversion of light energy into electrical signals. These devices hold promise for diverse applications, including optoelectronics, photovoltaics, and sensing, by leveraging the complementary properties of inorganic and organic semiconductors.

	370 (nm)	**450 (nm)**	**530 (nm)**	**630 (nm)**	**680 (nm)**
$I_{ph}(\lambda)$ **(A)**	1.7×10^{-7}	4.66×10^{-7}	3.75×10^{-7}	8.7×10^{-8}	6.17×10^{-8}
$S(\lambda)$	1300	3580	2880	668	474
$R(\lambda)$ $[\mathrm{A\,W^{-1}}]$	0.425×10^{-2}	1.165×10^{-2}	0.9375×10^{-2}	2.15×10^{-3}	1.54×10^{-3}
D* (Jones)	1.31×10^{11}	3.58×10^{11}	2.9×10^{11}	0.664×10^{11}	0.476×10^{11}
EQE (%)	1.42	3.21	2.19	0.42	0.28

Table 4.2: **Zero bias I-V parameters of ITO/ZnO/P3HT:Squaraine Dye/Ag device**

While analyzing the I-V data of the

ITO/ZnO/P3HT:Squarine dye blend/Ag hybrid photodetector, we observed a photovoltaic effect at wavelengths of 370 nm, 450 nm, 520 nm, 630 nm, and 680 nm, as shown in Figure4.5 . It was observed that the device exhibits a dark current of 1.31 $\times 10^{-10}$ A at zero bias.

In addition to analyzing the I-V results, we conducted further calculations to determine various parameters for the wavelengths of 370 nm, 450 nm, 520 nm, 630 nm, and 680 nm. These parameters include photo sensitivity, responsivity, specific detectivity, and external quantum efficiency (EQE). The corresponding values for each wavelength are summarized in the table 4.2.

4.4 Summary

The main goal of this research was to develop a hybrid photodetector that operates in the near-infrared (NIR) range and can be used in medical applications. The study focused on fabricating and evaluating the performance of these photodetectors by combining P3HT and Squaraine dye in a bulk heterojunction structure.

Blending Squaraine dye with P3HT resulted in significant enhancements in the photodetectors' photoresponse and the ability to tune their sensitivity to different wavelengths. The researchers characterized the electrical properties of the photodetectors using current-voltage curves under various illumination conditions.

The study also analyzed the photodetectors' response to different wavelengths and calculated key performance parameters such as photo sensitivity, responsivity, specific detectivity, and external quantum efficiency across a range of wavelengths from 370 nm to 680 nm. It was observed that the fabricated photodetectors exhibited broadband photodetection capabilities, covering the UV, visible, and NIR regions.

Furthermore, the researchers noted a favorable photovoltaic effect in the photodetectors across a wide range of wavelengths from 200 nm to 900 nm, which was attributed to the incorporation of Squaraine dye with P3HT. Hybrid photodetectors with P3HT and Squaraine dye exhibited improved performance, broad spectral response, high sensitivity, and tunable properties, thanks to the crucial role of the photovoltaic effect in converting light energy into electrical signals.

Chapter 5

Conclusions and Future work

5.1 Conclusions

In this study, our primary objective is to fabricate a hybrid NIR photodetector for healthcare applications. To achieve this, we embarked on a comprehensive investigation of the active semiconductor material properties and performed meticulous characterization studies.

Firstly, we successfully fabricated the ITO/ZnO/P3HT/Ag photodetector and meticulously analyzed its photoresponse across various wavelengths: 370nm, 450nm, 520nm, 620nm, and 680nm. Notably, we observed exceptional photoresponse in the UV-Vis region, particularly at 370nm, 450nm, and 520nm. The outstanding performance in the UV range was attributed to the presence of ZnO, while the enhanced photoresponse in the visible region was a result of incorporating P3HT. Furthermore, during our analysis of the IV characteristics, we made an intriguing observation—a photovoltaic effect was evident at 450nm and 520nm wavelengths. In summary, our device exhibited a self-biased photodetector behavior, specifically tailored for UV-Vis applications.

Moving forward, we proceeded to fabricate a photodetector with an ITO/ZnO/P3HT:Squaraine Dye Blend/Ag device structure. The incorporation of Squaraine dye was motivated by its impressive absorbance properties in the NIR region, aligning perfectly with our goal of developing a hybrid NIR photodetector. Remarkably, this device demonstrated a significant rectification ratio of approximately 218 and yielded photocurrents on the order of 10^2 to 10^3 . A notable advantage we discovered was the device's photovoltaic behavior, which spanned an impressive range of wavelengths from 200nm to 900nm. Specifically, we focused our investigation on key wavelengths—370nm, 450nm, 520nm, 630nm, and 680nm—to highlight the device's performance. Consequently, this particular photodetector showcased its prowess as a broadband UV-Vis-NIR self-biased photodetector, poised for a wide array of applications in healthcare and beyond.

5.2 Future scope of the work

There is significant potential for exploration and investigation in this work, offering a wide range of possibilities. Firstly, we need to focus on optimizing the blending ratio of P3HT and Squaraine dye to enhance the performance of the ITO/ZnO/P3HT:Squaraine Dye Blend/Ag hybrid photodetector device. By fine-tuning this ratio, we can achieve improved device characteristics and better overall performance.

Secondly, we can explore the implementation of ZnO nanorod structures in the fabrication of the ITO/ZnO Nanorods/P3HT:Squaraine Dye Blend/Ag device. This approach aims to reduce defect states and increase the interface area between ZnO and the P3HT:Squaraine dye blend. The anticipated outcome is enhanced charge transport and efficient exciton diffusion, ultimately leading to improved device performance. Thorough analysis and evaluation of the device performance will be crucial in this investigation.

Thirdly, we can investigate the impact of varying the molarity of the ZnO seed solution and controlling the thickness of the ZnO buffer layer on device performance. By carefully adjusting these parameters, we can identify an optimized ZnO buffer layer configuration that yields superior device performance. This analysis will provide valuable insights into the relationship between the ZnO buffer layer and device efficiency.

Additionally, we can explore the potential enhancement of hybrid photodetector efficiency through the incorporation of surface plasmon resonance. This technique aims to leverage the interaction between light and metal nanoparticles to further improve the performance of the photodetector. By investigating and analyzing the impact of surface plasmon resonance on device efficiency, we can uncover new avenues for improving device performance.

Furthermore, in the next phase of this work, we can incorporate different Squaraine dyes that exhibit strong absorption in the NIR region. By following the same thematic approach outlined above, we can develop superior NIR hybrid photodetectors with applications in healthcare and other fields. This opens up new possibilities for advancing the technology and expanding its potential impact.

Overall, this work offers ample opportunities for exploration and advancement, with the potential to make significant contributions to the field of hybrid photodetectors, particularly in the realm of healthcare applications.

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