PLASMONIC ENHANCED THIRD ORDER OPTICAL NONLINEAR PROPERTIES OF NANOSTRUCTURED CU_XO THIN FILM

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2025

PLASMONIC ENHANCED THIRD ORDER OPTICAL NONLINEAR PROPERTIES OF NANOSTRUCTURED CU_XO THIN FILM

by

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Thesis submitted in fulfilment of the requirements
for the degree of
Master of Science

February 2025

DEDICATION

This thesis is especially dedicated to all the martyrs from Palestine and Bangladesh in 2023-24. It is also dedicated to my beloved parents, my lone younger brother (Imran), my late grandparents, my whole family, and all my dearest friends and well-wishers.

Thank you all for your love and support.

ACKNOWLEDGEMENT

I would love to express my gratitude to ALLAH SWT for giving me such an opportunity and assisting me endlessly in finishing my master's thesis in "Plasmonic Enhanced Third Order Optical Nonlinear Properties of Nanostructured Cu_xO Thin Film"

I would love to extend my deepest gratitude and admiration to my master's supervisor, Dr. Sabah M. Mohammed, for his unwavering dedication and outstanding guidance during my studies. I received an immense amount of advice, support, and recommendations that improved even my personal life. I am thankful to my supervisor; whose great attention and support enabled this work to be finished within the stipulated time frame. I will always remember his tender affection for me. It will truly remain priceless throughout the rest of my life.

My profound appreciation and thanks go to my co-supervisor, Dr. Mundzir Abdullah, for his kind support and motivational leadership during this research project. His scientific advice in bolstering the task at hand is much appreciated. Discussions on different extraordinary, experimental, personal, and traditional topics have greatly supported my scholarly life, especially in nonlinear optics.

I express my sincere gratitude to the entire faculty at the Institute of Nano Optoelectronics Research and Technology (INOR), Nano Optoelectronics Research and Technology (NOR), and the Engineering Lab at Universiti Sains Malaysia (USM) for their invaluable cooperation and support in providing laboratory equipment necessary for my experimental work.

I would like to extend my sincere gratitude to my teammates, brothers and sisters from the INOR and the School of Physics, USM for their kind gesture and the amazing, unforgettable time spent with them.

I'm especially appreciative of my parents, whose encouragement and unwavering support are an eternal source of inspiration for me. I am appreciative to my only younger brother, Mr. Imran Nazir, for his kindness, affection, and promptness.

It gives me great pleasure to thank all my Bangladeshi and International friends, particularly Mr Raja Aqib Shamim, Mr Ravi Sanker Bharma, Mr Muhammad Amir, Mr Abdul Shekkeer K M, and Saleh Karama Obaid Alsaee, Guo Xiang, Atia sharif, Iqra Maqsood and many more for their unwavering faith in me and their appreciations. Their affection, concern, and encouragement during my hectic research schedule assisted and inspired me to complete my Master's journey.

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LIST OF SYMBOLS

A	Absorbance
D	Crystallite size
k	Scherrer constant
λ	X-ray wavelength
β	Full width at half maximum
θ	Bragg diffraction angle
δ	Dislocation density
ε	Lattice strain
I_o	Light intensity
I	Transmitted light
ϵ	Molar absorptivity
c	Concentration of the sample
E_g	Energy band gap
T	Transmittance
hv	Photon energy
α	Absorption coefficient
P	Polarization
E	Electric field
ϵ_o	Permittivity
χ	Nonlinear optical susceptibility
n_2	Nonlinear refractive index
n_o	Nonlinear refractive index
β	Nonlinear absorption coefficient
q_o	Curve generating value
Z_R	Diffraction length

k	Wave vector
L_{eff}	Effective thickness of the sample
L	Thickness of the sample
c	Speed of light in the vacuum

LIST OF ABBREVIATIONS

Ag	Silver
AFM	Atomic Force Microscopy
Au	Gold
CBD-NPs	Chemical Bath Deposition of Nanoparticles
CW	Continuous Wave
Cu	Copper
DC	Direct Current
DFWM	Degenerate Four-Wave Mixing
DW	Deionized Water
EDX	Energy Dispersive X-ray spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
FWHM	Full Width Half Max
HILs	Hole Injection Layers
$^{\bullet}HO$	Hydroxyl Radicals
IR	Infrared
LUMO	Lowest Unoccupied Molecular Orbital
LSPR	Localized Surface Plasmon Resonance
MTO	Metal Oxide
NLA	Nonlinear Absorption Coefficient
NLO	Nonlinear Optics
NLR	Nonlinear Refractive Index
NPs	Nanoparticles
NIR	Near-Infrared Radiation
OLED	Organic Light-Emitting Diodes
PLAL	Pulsed Laser Ablation in Liquid
PSI	Pound Per Square Inch
RF	Radio Frequency
SHG	Second Harmonic Generation
sccm	Standard Cubic Centimeters Per Minute
RT	Room Temperature
SPR	Surface Plasmon Resonance

THG	Third Harmonic Generation
TLM	Thermal Lensing Model
UV	Ultraviolet
Vis	Visible
XRD	X-Ray Diffraction
2D	Two-Dimensional
3D	Three-Dimensional
INOR	Institute of Nano Optoelectronics Research and Technology
USM	Universiti Sains Malaysia

SIFAR OPTIK TAK LINEAR TAHAP KETIGA YANG DIPERTINGKATKAN MELALUI PLASMONIK BAGI FILEM NIPIS CU_XO

ABSTRAK

Tesis ini meneroka aplikasi optik tak linear (NLO) tahap ketiga menggunakan oksida logam peralihan yang dirawat secara haba, khususnya oksida kuprum (Cu_xO) (termasuk Cu_2O, CuO, dan Cu_4O_3). Kajian ini turut melibatkan logam adi seperti emas (Au) dan perak (Ag), serta kombinasi (Au+Ag) dengan Cu_xO untuk meningkatkan sifatnya. Logam adi dan nanostruktur plasmoniknya telah banyak dikaji kerana ciri-ciri optiknya yang unik dan aplikasi dalam pelbagai bidang sains. Ciri-ciri optik tak linear seperti penyerapan tak linear (NLA), β, pembiasan tak linear (NLR), n_2, dan kerentanan tak linear optik (NLO susceptibility), $[\chi^{(3)}]$ bagi semua sampel yang disediakan ditentukan menggunakan laser gelombang berterusan (CW) pada panjang gelombang 637 nm melalui teknik Z-scan pancaran tunggal. Tiga model digunakan untuk mencapai objektif kajian dan memperkenalkan pengetahuan baharu. Model pertama melibatkan pemeriksaan tindak balas optik tak linear tahap ketiga bagi filem nipis Cu_xO yang dioksidakan secara semula jadi di udara dan kemudian dirawat haba pada pelbagai suhu. Filem ini dihasilkan menggunakan sputtering DC reaktif. Magnitud optimum kerentanan tak linear tahap ketiga, $[\chi^{(3)}]$ bagi filem nipis Cu_xO selepas rawatan haba diukur pada nilai $41.86 \times 10^{-3}\ esu$ pada suhu 450°C. Dalam model kedua, ciri-ciri optik tak linear bagi cecair/larutan logam adi emas (Au), perak (Ag), dan kombinasi (Au+Ag) nanopartikel (NPs) disiasat. Nanopartikel ini disintesis melalui kaedah mesra alam pelaseran denyutan dalam cecair (PLAL). Walaupun keputusan menunjukkan nanopartikel Au yang disediakan mempunyai sifat optik tak linear tertinggi, kombinasi bimetalik (Au+Ag) NPs masih merupakan calon yang

berpotensi untuk pembangunan aplikasi fotonik tak linear berprestasi tinggi. Dalam model ketiga dan terakhir, pengarang memperluaskan dan menunjukkan kajian dalam meningkatkan tindak balas optik tak linear tahap ketiga filem nipis Cu_xO dengan menyelapisinya menggunakan nanopartikel plasmonik adi seperti Au, Ag, dan kombinasi (Au+Ag), yang disintesis melalui teknik penyalutan kimia kos rendah (CBD-NPs). Magnitud maksimum kebolehan tak linear tertib ketiga, $[\chi^{(3)}]$ dianggarkan pada nilai $44.09\, x10^{-3}\, esu$ bagi filem nipis (Au+Ag)/Cu_xO, yang merupakan nilai tertinggi yang diperoleh di antara semua spesimen yang disediakan.

PLASMONIC ENHANCED THIRD ORDER OPTICAL NONLINEAR PROPERTIES OF NANOSTRUCTURED CU_XO THIN FILM

ABSTRACT

This thesis explores the third-order nonlinear optical (NLO)-based applications using thermally treated transition metal oxides, specifically copper oxides (Cu_xO) (including Cu_2O, CuO, and Cu_4O_3). The study incorporates noble metals like gold (Au), and silver (Ag), and their (Au+Ag) combinations with the Cu_xO to enhance their properties. Noble metals and their plasmonic nanostructures are well-studied for their unique optical characteristics and applications across various scientific fields. The nonlinear optical characteristics like the NLA, β, the NLR, n_2, and the NLO susceptibility, $[\chi^{(3)}]$ of all prepared samples were determined by using the continuous wave (CW) laser at 637 nm wavelength via the single beam Z-scan technique. Three models were used to achieve the research objectives and introduce new knowledge. The first model involved examining the third-order nonlinear optical response of Cu_xO thin films, which were naturally oxidized in air and then heat-treated at various temperatures. These films were created using reactive DC sputtering. The optimal magnitude of third-order nonlinear susceptibility, $[\chi^{(3)}]$ of post-annealed Cu_xO thin film was measured to be $41.86\ x10^{-3} esu$ at 450°C temperature. In the second model, I investigate the nonlinear optical properties of liquid/solution of noble metal Gold (Au), and Silver (Ag) NPs, and their (Au+Ag) combinations, synthesized via the eco-friendly pulsed laser ablation in liquid (PLAL) method. Although, the results show that the prepared Au NPs demonstrate the highest optical nonlinearities but still it implies that the combined (Au+Ag) bimetallic NPs are a promising candidate for the development of high-performance nonlinear photonic applications. In the third and

final model, I have expanded and demonstrated his work in enhancing the third-order nonlinear optical response of Cu_xO thin films by coating the plasmonic noble NPs, such as Au, Ag, and their (Au+Ag) combination, synthesized by the cost-effective chemical bath deposition of nanoparticles (CBD-NPs) technique. The determined maximum magnitude of the third-order NLO susceptibility, $[\chi^{(3)}]$ was estimated as $44.09\ x10^{-3} esu$ for (Au+Ag)/Cu_xO thin film, which was the highest obtained value of the NLO susceptibility, $[\chi^{(3)}]$ among all prepared specimens.

CHAPTER 1

INTRODUCTION

Thin films of transition-metal oxide (TMO) have shown great promise as nonlinear optical materials owing to their tremendous optical nonlinearity, rapid response times, and strong chemical and thermal stability. A common limitation of metal/dielectric composite films' performance is resonance absorption, which can result in heat damage and light loss even though these films have shown notable third-order nonlinear optical effects[1, 2]. Copper oxide (Cu_xO), one of the TMOs, has attracted significant interest considering its possible uses in gas sensors, memory devices, capacitors, energy storage applications and high-temperature superconductors[3-7]. Previous investigation has documented notable third-order nonlinear susceptibilities, $\chi^{(3)}$ in a range of TMO films, such as those composed of CdO, V_2O_5, Co_3O_4, Cr_2O_3, Fe_2O_3, and Mn_3O_4[8-10]In this context, an extensive understanding of the third-order nonlinear response of Cu_xO thin films is still essential for the utilization of different real-life applications such as all-optical switching and optical power limiting systems, optical data storage, and many more.

The distinctive combination of both structural and compositional properties in bimetal or bimetal oxide nanostructures enables the further demand for higher-performance active materials beyond monometallic nanostructures[11]. Of those, the semiconductor thin films that are enhanced with the nobler metal nanoparticles (NPs) such as Au and Ag show a remarkable advantage due to their outstanding optical and electrical properties. Noble metal nanoparticles (NPs), such as Au and Ag, demonstrate unique absorption like Localized Surface Plasmon Resonance (LSPR) in the visible range of the electromagnetic spectrum[12, 13]. This phenomenon is caused by the resonant oscillation of the free electrons in the NPs upon light irradiation. Plasmonic

metal-semiconductor hybrid nanostructures offer a variety of advantages: They allow for the coupling of different plasmonic characteristics considering semiconductors may also demonstrate plasmonic absorption with the right concentration of free carriers, like free holes in the valence band, and metal NPs can exhibit plasmonic behavior through surface free electron oscillation[14-16]. These hybrids also help with charge redistribution between the metal and semiconductor, where the abundant free electrons in the metal can transfer rapidly to the lowest unoccupied molecular orbital (LUMO) of the semiconductor, developing a region with a high charge density close to the metal-semiconductor interface[16]. They allow the formation of multimodal plasmonic absorptions, since, in contrast to conventional semiconductor nanoparticles, which usually absorb light in the ultraviolet region, the LSPR peaks of metal nanostructures can be tuned to the near-infrared (NIR) region through elemental or morphological modifications. This plasmonic metal and semiconductor integration provides a hybrid nanoscale entity with a sophisticated optical absorption characteristic[16, 17]. The development of enhanced nonlinear optical characteristics can be facilitated by metal-semiconductor hybrid nanostructures, as these advantages demonstrate.

1.1 Problem Statements

The evolution of high-efficiency third-order optical nonlinear devices remains a significant challenge in photonics and optoelectronics fields. While numerous investigations have been conducted, there is still a pressing need for techniques for developing these devices in a simple, cost-effective, and more efficient manner. The Z-scan method has emerged as a straightforward, noteworthy, and inexpensive method for characterizing the organic, inorganic, metal, and nonmetal semiconductor materials

used in applications such as optical limiting, all-optical switching, and optical data storage. However, the effectiveness of these applications is often limited by the certain physical properties of the materials, particularly their structural and optical characteristics, including the thermal impact as the temperature influences the Z-scan curves such as NLA and NLR[18-21].

For possible use in the field of photonic and optoelectronic applications, Cu_xO thin film exhibits promising optical and electrical properties with a tuneable electronic transitional nature[22-24]The impact of annealing treatment on naturally oxidized CuxO thin films, especially in an N_2 atmosphere, and its effect on third-order nonlinear optical responses remain underexplored. Understanding how temperature variations during thermal treatment influence both linear and nonlinear optical properties is crucial for realizing their full potential.

Concurrently, noble metal nanoparticles, particularly Au and Ag, exhibit unique surface plasmon resonance (SPR) absorption in the visible region of the electromagnetic spectrum. The SPR effect in these nanostructures produces a strong local field on their surface and in the immediate vicinity, making them attractive for different practical applications. By tuning parameters like size, shape, and the surrounding dielectric medium, these nanoparticles can be controlled throughout an extensive range, from UV to near-infrared[25]. Nanostructures' surface plasmon resonance (SPR) causes a strong local field on the surface and near the surrounding nanostructures. Many practical applications of this kind of system are built around the plasmonic band effect and its unique characteristics. SPR band fine-tuning is essential for many of these applications, and it can be addressed by controllably altering the bands' morphological characteristics and/or composition[26]. This study also focuses on how noble NPs such as Au and Ag impact naturally oxidized Cu_xO thin films

towards the third-order NLO properties. This research aims to consider the following objectives addressed in section 1.2.

By, this thesis, I seek to contribute to developing more cost-effective and efficient third-order nonlinear optical devices, potentially advancing the field of photonics and optoelectronics.

1.2 Thesis Objectives

The primary objectives of this thesis work can be summarized in the following points:

1. To investigate the effects of annealing temperature on the optical and structural properties of naturally oxidized Cu_xO thin films and its implications for third-order nonlinear optical (NLO) properties
2. To study the third-order nonlinear optical behaviour of noble metal NPs such as Au, Ag NPs, and their combined (Au+Ag) bimetallic NPs, synthesized PLAL technique.
3. To study the third-order optical nonlinear response of plasmonic enhanced nanostructured Cu_xO thin films coated by noble metal NPs such as Au, Ag NPs, and their combined (Au+Ag) bimetallic NPs.

1.3 Research Originality

The originality of this thesis work is attributed to the following aspects:

1. The effective development of naturally oxidized Cu_xO (Cu_2O and CuO phases) thin films on glass substrates formed by natural air conditions, then thermally annealed under N_2 ambient at various temperatures with

extremely small diameters (<100 nm) and excellent structural and optical properties.

2. The successful PLAL technique-based synthesis of highly-plasmonic and high-density Au and Ag NPs into deionized water (DW) and the enhancement of highly-plasmonic and high-density monometallic Au and Ag NPs and their combined (Au+Ag) bimetallic NPs onto naturally oxidized Cu_xO (CuO and Cu_4O_3 phases) thin films on the glass substrate using the low-temperature CBD-NPs technique for the first time, to the best of my knowledge.
3. The study of the annealing effect on third-order NLO properties along with the structural and linear optical properties of naturally oxidized Cu_xO thin films on glass substrates subjected to heat treatment under N_2 ambient at different temperatures, for the first time, to the best of my knowledge.
4. The study of the third-order NLO characteristics including the morphological, compositional, topological, structural, and linear optical behaviours of highly-plasmonic monometallic Au, Ag NPs, and their combined (Au+Ag) bimetallic NPs incorporated naturally oxidized Cu_xO thin films, for the first time, to the best of my knowledge.

1.4 Thesis Organization

Chapter 1 presents a brief introduction to Cu_xO, Au, and Ag nanostructures, as well as the problem statement, thesis objectives, and originality of the thesis.

Chapter 2 discusses the literature review and theoretical fundamental attributions, such as structural and optical properties and applications of CuxO, Au, and Ag

nanostructures. It also describes the growth techniques and briefly describes the thermal annealing process.

Chapter 3 discusses the general principles of different growth techniques for prepared thin films and nanoparticles and describes the equipment employed to characterize all prepared specimens.

Chapter 4 includes the results related to the deposition and characterizations of all prepared thin films, nanoparticles (i.e. Cu_xO thin films, Au, Ag, and combined (Au+Ag) bimetallic NPs), and the synthesized NPs enhanced thin films (i.e. Au/Cu_xO, Ag/Cu_xO, and Au+Ag/Cu_xO thin films). Included are results on the properties of morphology, compositional, topological, structural, linear optical, and nonlinear optical characteristics.

Finally, the conclusions of this thesis and recommendations for future works are discussed in Chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Third-order nonlinear optics (NLO) involves the interaction of light with a medium in which the polarization P of the material responds non-linearly to the applied electric field E. The first noteworthy discovery related to third-order nonlinear optics was the observation of third-harmonic generation (THG) in 1965 by Maker and Terhune in calcite[27].

This chapter provides knowledge of the underlying theories and concepts of each topic discussed in this work. It begins with the basic characteristics of Cu_xO, such as its electrical structure, optical characteristics, and crystal structure. Along with them, several fabrication methods and the range of Cu_xO applications are also covered. This chapter also addresses the fundamental attributes of high-plasmonic Au and Ag NPs, their optical properties, production process, electrical band structure, and potential applications. At the end of this chapter, I also briefly represent the third-order NLO studies including its origin, which was my studies' primary focus.

2.2 Fundamental Attributions and Applications of Cu_xO

This section primarily focuses on the fundamental characteristics of nanostructured Cu_xO, including its crystal structure, optical properties, and electronic band structures. It also delineates the impact of impurities or doping on these characteristics.

2.2.1 Crystal Structure of Cu_xO

One s-orbital electron on top of a filled d-electron shell characterizes Copper (Cu) metal[28], which is found in three oxidation phases: copper (II) oxide (CuO), copper (I) oxide (Cu_2O), and copper (I, II) oxide mineral (Cu_4O_3). copper (II) oxide (CuO) is also known as the Cupric Oxide or as Tenorite. All the schematic crystal structures of CuO, Cu_2O, and Cu_4O_3 phases of Cu are illustrated in Figure 2. 1 (a), (b), and (c), respectively.

Copper (II) oxide (CuO) has a black solid appearance that comes with a monoclinic crystal structure. CuO is a stable phase of Cu that exhibits p-type conductivity. In the CuO phase of Cu, structurally, four coplanar oxygen atoms at a rectangular parallelogram's corners coordinate with copper atoms to form chains via sharing edges. At the corners of a warped tetrahedron, four copper atoms are coordinated with one oxygen atom[29, 30].

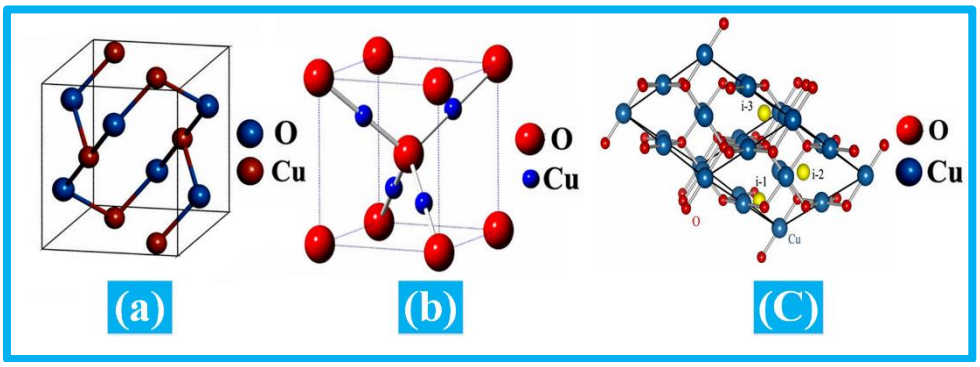

Figure 2. 1 Schematic crystal structure of (a) CuO[31] (b) Cu_2O[32], and (c) Cu_4O_3[33]

Copper (I) oxide (Cu_2O) is also known as cuprous oxide, another inorganic and one of the most studied compounds of Cu. Cu_2O is a reddish solid in color that belongs to a cubic structure with a lattice constant of 4.2696 Å. Structurally, in a cubic arrangement, each copper atom is bonded to two oxygen atoms, and each oxygen atom is tetrahedrally coordinated with four copper atoms[34, 35]. Cu_2O also demonstrates a p-type conductivity. Copper (I, II) oxide mineral (Cu_4O_3) is the third phase of Cu,

known as the paramelaconite. Cu_4O_3 is the most metastable phase, and it acts as the intermediate characteristic of Cu's CuO and Cu_2O phases owing to its similar crystallinity. Cu_4O_3 has an atomic ratio of 1.33 and a lattice constant of a = 5.837 Å and c = 9.932 Å, which correspond to a tetragonal structure[36]. Various materials with the required physical, electrical, and optical properties to produce modern devices are crucial given the rapid evolution of electronics.

For this reason, researchers are focusing an increasing amount of their attention on studying known and novel chemical compounds that possess semiconductor qualities. Metal oxides are among these substances that show the greatest promise[37]. While making sensors, detectors, photovoltaic devices, and other devices, these materials have several benefits over most other compounds. These benefits, which enable the direct acquisition of materials from the environment, include chemical stability, non-toxicity, and environmental safety[38, 39].

2.2.2 Liner Optical Properties of Cu_xO

Nanostructured Cu_xO (CuO, Cu_2O, and Cu_4O_3) thin films are one of the potential transitional metal semiconductor materials. These nanostructured thin films are outstanding for optoelectronics and photonic applications due to their p-type conductivity and exceptional optical properties[40]. The Cu_2O has an exceptionally high exciton binding energy of 150 meV for the 1s exciton[41]. This is significantly larger than most other semiconductors, making Cu_2O an interesting material for exciton studies, while Cu_4O_3 demonstrates a small exciton binding energy[42]. The pure CuO phase of Cu reveals a wide absorption peak at 240 nm[43], and the nanostructured Cu_2O phase demonstrates an absorption peak at around 270 nm and 340 nm[44]. Besides this, according to the IR transmission measurements, it is also known that the absorption

bands of CuO and Cu_2O phases thin film appear around 532 cm^{-1} and 615 cm^{-1}, respectively[45, 46].

2.2.3 Electronic Band Structure of Cu_xO

In solid-state physics, energy band theory is an effective tool for comprehending the electrical characteristics of materials[47]. It describes the allowed energy ranges for electrons, which are grouped into bands and divided by allowed gaps. The energy band gap, (E_g) is the difference, as illustrated in Figure 2. 2, between the valence band's highest energy level and the conduction band's lowest energy level. Metals are electrically conductive because of their partially filled band. On the other hand, semiconductors exhibit an empty conduction band and a full valence band that is divided by the energy band gap[48]The conditions that stimulate electrons across this gap significantly impact semiconductor conductivity. Compared to semiconductors, insulators have a wider band gap, which makes it more difficult to excite electrons and causes them to behave insulatingly.

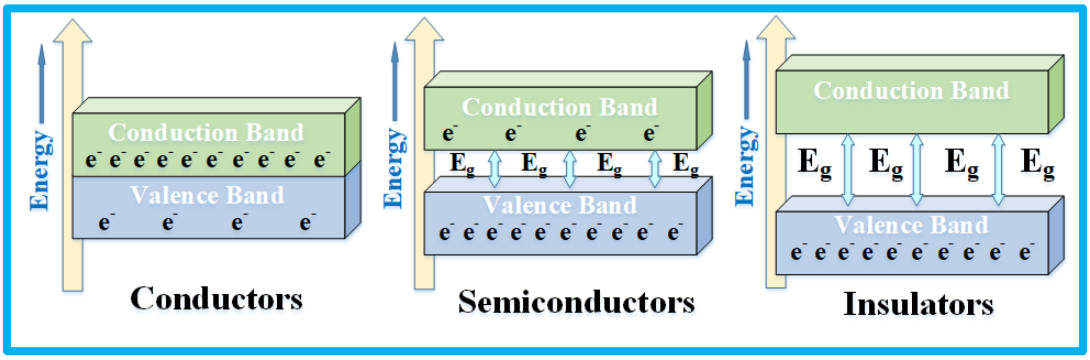

Figure 2. 2 Schematic diagram of the energy band gap of conductors, semiconductors, and insulators

Two types of energy band gaps are (E_g) in crystalline semiconductor materials: direct band gaps and indirect band gaps. Both CuO and Cu_2O phases are the most stable phases of Cu and exhibit a direct electronic transition nature (energy band gap) with a range of 1.2 eV to 2.1 eV and 2.2 eV to 5.4 eV (tuneable), respectively[49, 50]. This

thesis study investigated the optical absorption and transmission spectra of the obtained CuxO thin films using an Agilent Technologies Carry 5000 UV-Vis spectrophotometer. The employed wavelength range was fixed at 200 nm to 1000 nm. Furthermore, Tauc's plot method was implemented to identify the energy band gaps of all prepared Cu_xO thin films from the obtained transmission data.

2.2.4 Applications of Cu_xO

Cu_xO has been implemented in numerous applications, from optical devices to outstanding thermally conductive systems. This section discusses some of the most popular advancements that may be achieved by using nanostructured Cu_xO phases.

Cu_xO is a desirable semiconductor material for photodetectors owing to its exceptional optoelectronic attributes and comparatively small band gap[51]. Cu_xO presents a significant deal of promise for the fabrication of inexpensive, highly effective sensors that allow for sensing based on photoluminescence, refractive index alterations[52]. This covers gas, optical, and biological sensors. Photodetectors are useful tools that have a wide range of uses, such as ozone layer monitoring, free-space communications, navigator assistance, and thermal imaging systems[53]. Cu_xO also presents a promising avenue for developing semiconductor-based gas sensors with extremely high sensitivity. By reducing the size of Cu_xO to nanoscale dimensions—roughly twice the Debye length—and adding the right dopants, its sensing capabilities can be enhanced[54]. The Cu_xO surface's adaptability is further enhanced by highly plasmonic Nanoparticles (NPs) notably Au[55, 56], and Ag[55, 57] which are linked to it, mostly through their spill-over effects.

The development of solar applications is gaining more attention because of the necessity and demand for a cost-effective, clean energy source. Cu_xO films have great potential for developing dye-sensitized and heterojunction-based solar cells and organic

light-emitting diodes (OLED). Cu_xO has garnered significant attention as a metal oxide material for solar energy applications based on its theoretical power conversion efficiency (PCE) of 20% to 29%[58] and better absorption coefficient than single-crystalline Si[59].

Besides this, Organic Light-Emitting Diodes (OLEDs) have also been equipped with Cu_xO[60]. Optimizing carrier injection capabilities at the interface between the active layer and anode materials is crucial for building effective OLEDs. As Hole Injection Layers (HILs) reduce the hole injection barrier, Cu_xO films are frequently employed[61, 62]. According to Kim et al., optimizing OLED performance can be achieved by utilizing a mixed stoichiometry of CuO and Cu_2O[63]. On the other hand, Cu_xO is a low-cost, small-energy band gap photocatalyst that shows promise in a variety of chemical processes, including the breakdown of organic contaminants and water splitting under visible light irradiation[51, 64].

When exposed to light, Cu_xO creates electron/hole pairs that can react with water to produce hydroxyl radicals ($^{\bullet}HO$). Mineralizing most organic compounds is possible with this radical[65, 66]. When it comes to water splitting applications, the photogenerated electrons, which make up the minority charge carriers of Cu_xO, reduce water to hydrogen gas (H_2), while the holes, which make up the majority charge carriers, oxidize water to oxygen gas (O_2)[67, 68]. It's important to note that sunlight can make H_2 from water because the Cu_xO conduction band is more negative than the H^+/H_2 redox potential. In addition to the described applications in section 2.7, numerous further applications of nanostructured Cu_xO have been documented. It is noteworthy that supercapacitors and ceramic resistors have both utilized nanostructured Cu_xO[69, 70]. Furthermore, thin-film transistors[71], electrochromic[72], electrochemical[73],

antimicrobial[74], heterogeneous catalysis[75] and so on. Of course, Cu_xO has been applied in other contexts, but they are outside the purview of this study.

2.3 Synthesis Methods of Cu_xO

Nowadays, reactive sputtering, anodizing, chemical vapour deposition, and thermal oxidization are some of the techniques used for fabricating copper oxide thin films[76]. Sputtering is a common technique for thin film deposition because it involves blasting ions onto surface atoms to transfer the electrode material. This technique assists in generating electrode material vapour as a byproduct[77]. Besides this, this technique concludes in the presence of reactive gases using reactive sputtering, which has several advantages, particularly when combined with a metal cathode: it results in a "high-rate, controlled formation"[77].

Another technique to fabricate oxide thin films is called anodizing. It works by generating a DC discharge[78] with the aid of the substrate and an oxygen atmosphere; the reaction happens as a result of electrons and negative oxygen ions bombarding the surface[77]. The creation of "very dense, defect-free, amorphous oxide films" is the primary advantage of this process[77]. The disadvantage of this approach, specifically for my research project, is that anodizing is more effective on valve metals—which exclude copper.

One advantage of thermal oxidation is that it produces "very high purity oxide films," much like Chemical Vapor Deposition (CVD). It likewise utilizes a gas phase, with the oxide resulting from the substrate[79]. It's regarded as one of the most straightforward methods for producing metal oxide nanostructure. Nonetheless, this technique is most effective for silicon and requires significantly higher temperatures,

typically from 7000°C to 12000°C with the presence of steam[79]. In these circumstances, the deposition of copper is not as effective as the sputtering method.

The sputtering process is a phenomenon that involves the physical vapor deposition (PVD) of the target material (metal or oxide) in thin films onto a substrate (such as a glass or Si wafer). It is claimed that thin films developed in a vacuum for the first time since W. R. Grove discovered a sputtering phenomenon in 1852(J. T. Gudmundsson et al)[80]. A high vacuum (pressure of not more than 10^{-6} mbar) is produced inside the deposition chamber after the target and sample substrate have been loaded[81]. Figure 2. 3 (a) and (b) illustrate the schematic diagram of the DC sputtering chamber and an actual image of the employed sputtering chamber along with the Cu target and glass substrates, respectively.

Typically, Argon (Ar), a chemically inert gas, is carefully purged into that high-vacuum chamber with the aid of a mass-flow controller. The target material is deposited at the cathode, which receives a high electric voltage (RF or DC)[82]One electron is lost within the chamber, creating Ar plasma that is accelerated and directed toward the target. These high-energy Ar ions will lift some of the target's surface atoms through momentum transfer. Together, these released atoms and argon ions produce plasma, which moves in the direction of the substrate before being deposited there. Achieving a high vacuum and improving the target atoms' adherence to the substrate requires thorough cleaning of both the substrate and the chamber.

Various magnetron sputtering deposition techniques have been used to fabricate nanostructured materials such as reactive DC magnetron, RF magnetron, Ion-beam magnetron, and so on[83]. The researchers have shown great interest in DC sputtering as it is much easier to design and produce, this method is significantly cheaper than RF sputtering. The size of the target determines the DC power usage. Metal, alloy, and

complex nanostructure deposition are typically accomplished via Direct Current (DC) magnetron sputtering[84]. Hereby conducting materials are deposited using the DC sputtering technique using a magnetron.

In this context, the sputter target is exposed to a DC voltage, usually from -2 V to -5 kV. The target is struck by ionized Ar atoms, which are electrically neutral. Atoms are ejected from the target surface due to the high-energy collision and travel towards the substrate. The magnetron's magnetic field traps the electrons close to the target surface, which enhances sputtering gas ionization and raises the rate of thin film deposition. In addition to the sputtering gas (Ar), a reactive gas, like nitrogen (N_2) or oxygen (O_2), is also purged into the chamber. Target metal atoms and oxygen combine to generate the appropriate metal oxide at the substrate. I refer to this process as magnetron-reactive sputtering.

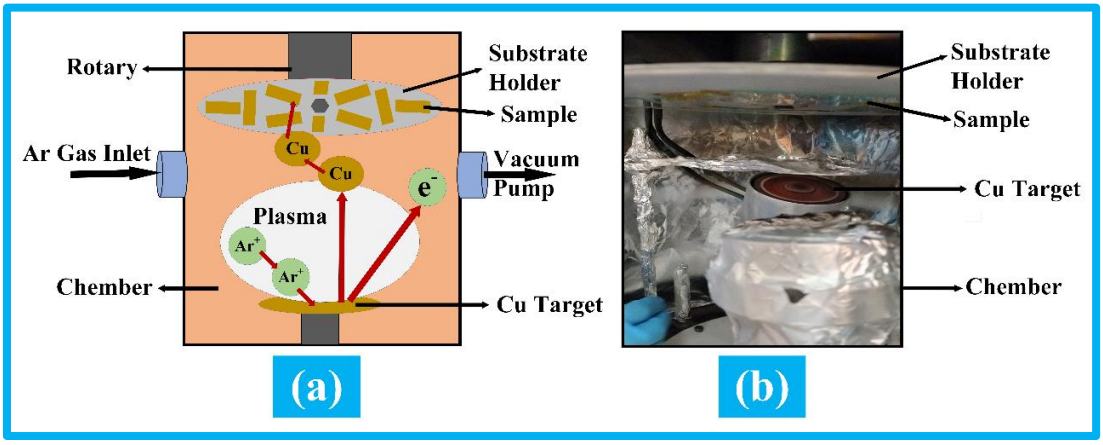

Figure 2. 3 (a) Schematic diagram of the DC sputtering chamber, and (b) actual image of the employed sputtering chamber

In this thesis project, I employed the reactive DC sputtering to deposit the copper-based thin film on the glass substrate from the Cu via a highly pure (99.99%) Cu target, where the used active sputtering gas was Ar, and the reactive gas was N_2. In further, the samples were then exposed to ambient air for 5 days to achieve a native Copper Oxide (Cu_xO) layer on the fair, uniform, and smooth-surfaced glass substrate[85, 86].

2.4 Thermal Annealing Process

The post-deposition heat treatment known as "thermal annealing" modifies the physical characteristics of the deposited materials (including their hardness). Post-annealing is an important fabrication process for improving the growth characteristics of different thin films. Grain growth, recrystallization, and recovery are the three phases of the annealing process. The first stage of eliminating internal instability, dislocations, and crystal defects causes the material to become flexible. All annealing treatments that occur before the formation of new grains are included in this first step of grain growth. New grains germinate and grow to replace the ones that have been distorted by internal forces in the following stage. Grain growth occurs if annealing is continued after recrystallization is finished. At this point, the microstructures begin to expand, which could result in the material's mechanical properties being inadequate.

Moreover, introducing various gases in the annealing chamber facilitates the changes in the optical thin film's properties. Surface roughness, the development of particular structural phases, crystallinity, grain size, and altered absorption/transmission regions or percentages are a few of these film qualities that can be enhanced. All of the thin films were produced by methodically annealing at various temperatures between 250°C and 550°C degrees for 30 minutes in a compact tabular furnace under a nitrogen (N_2) environment. The gas flow into the heat treatment furnace was maintained at a constant pressure of 5.00 PSI for all prepared thin films.

2.5 Fundamental Properties of Au and Ag NPs

This section's main focus is on the basic properties of high-plasmonic, nanostructured Gold (Au) and Silver (Ag) Nanoparticles (NPs), such as their crystal

structures, Optical behavior, and electrical band structures. The impact of contaminants or doping on the characteristics of Au and Ag NPs is also discussed in this section.

2.5.1 Crystal Structure of Au and Ag NPs

The transition between the valence and conduction bands is the only factor affecting optical characteristics like optical emission and absorption. Similar to other metals, noble metals have unbounded electrons. They become excellent conductors due to the cloud that surrounds the atomic nucleus. These particular properties also impact the optical qualities. Petr Slepicka et al. mentioned in their work that since the 17th century, researchers have been studying Au NPs[87]. The first scientific study on their fabrication and characteristics was presented by Faraday in 1857[88]. Recently, one of the most exciting developments in contemporary nanoscience and nanotechnology is the use of Au NPs. In recent years, researchers have shown tremendous interest in Au colloids due to their distinguishing optical, catalytic, and bio-functional strengths[89-91]. Au NPs demonstrate a spherical form, are an unsatisfied d-sub (5d) shell metal that demonstrates a Face-Centered Cubic (FCC) crystal structure and has five different oxidation states. Qifeng Ruan and colleagues claimed that the structure of Au nanospheres with a diameter ranging from 20 nm to 220 nm[92]. Au NPs have found extensive uses in the disciplines of physics, chemistry, electrochemical sensors, material science, catalysis, and biomedicine due to their attractive electronic, optical, magnetic, thermal, and catalytic characteristics[93-95].

Conversely, Ag NPs are among the wide range of nanomaterials that are now being explored and have been examined the most because of their practical utility in many contemporary applications. Ag NPs have a lengthy history[96], but their distinctive and intriguing physicochemical features are what first led to their current application. H. Chang et al. discussed that one of the first documented uses of Ag NPs

was as a color additive in the Lycurgus cup (c.a., 400 C.E.)[97], which produces the distinctive green-to-red color shifts as light passes through it. Scientists' interest in synthesizing Ag nanoparticles has increased recently due to its distinctive characteristics, which include chemical stability, excellent conductivity, catalysis, and most importantly, antibacterial activity[98, 99]. Ag NPs exhibit a spherical shape that a 4d metal that also demonstrates a Face-Centered Cubic (FCC) crystal structure[100]. Colourimetric, surface-enhanced Raman spectroscopy, fluorescence, and chemiluminescence sensors are among the sensors that use Ag NPs, while ammonia, heavy metals, and pesticides are among the discharged pollutants that these sensors detect in the environment. Besides this, Ag NPs have also aided in early identification, which has shortened the amount of time it takes to treat diseases like cancer.

2.5.2 Plasmonic Properties of Au and Ag NPs

The strong interaction between the nanoparticles' conduction electrons and incident light under particular resonance conditions is the Local Surface Plasmon Resonance (LSPR) source for noble metal NPs. These LSPR properties are another unique feature of noble metals that are convenient for researchers in developing different cutting-edge optoelectronic devices[101, 102]. Gold (Au) and Silver (Ag) NPs are incredibly efficient at scattering and absorbing light. For highly plasmonic NPs like Au, and Ag, the corresponding plasmon peak lies in the visible range (380 nm - 550 nm)[103, 104]. NPs with their LSPR in the ultraviolet (UV) range include Ru, Rh, Pd, and Pt. The LSPR wavelength is primarily determined by the composition of the metal. The size and crystallinity of the NPs also facilitate the ability to tune the LSPR wavelength and intensity[105]. A shift in the SPR of the electromagnetic wavelength towards the infrared portion of the electromagnetic spectrum is another effect of altering their particle size. Furthermore, the nonlinear optical enhancement of metallic

nanoparticles has also been associated with the optical excitation of the LSPR of the particles that may be employed in the field of various optical sensors[106, 107].

2.6 Synthesis Methods of High Plasmonic of Au and Ag

2.6.1 Pulsed Laser Ablation in Liquid (PLAL)

A materials synthesis method titled Pulsed Laser Ablation (PLA) involves removing a volume of material utilizing a pulsed laser that interacts with the bulk material and is distinguished by its power density, pulse duration, and repetition rate. PLA is considered the most versatile and promising approach due to its ability to ablate a wide variety of materials at extremely high energy densities. In 1987, Patil and colleagues reported the first study on the practical usage of pulsed laser ablation methods[108]. In the Pulsed Laser Ablation in Liquid (PLAL), the energy of laser photons converts into electrons on the target's surface and diffuses into the material. When focused on micron levels, the laser heats the material to a threshold temperature, speeding up vaporization and producing plasma. Following its formation, the plasma proceeds to react with liquid. As the plasma expands and cools, particles can emerge between nanometre and micrometre sizes. The schematic development of laser ablation in liquid is depicted in Figure 2. 4. "Laser-induced plasma" is the term used to describe first-formed plasma by the laser beam; Figure 2. 4 (a) illustrates this. The term "laser-induced plasma" refers to plasma that a laser has increased because the laser has produced more energy[109]. Put another way, the laser first creates plasma at the liquid-solid contact, which then spreads and produces larger plasma. At a nanoscale time range, four chemical processes occur inside the plasma and the liquid-plasma interface layer following plasma-induced plasma[110].

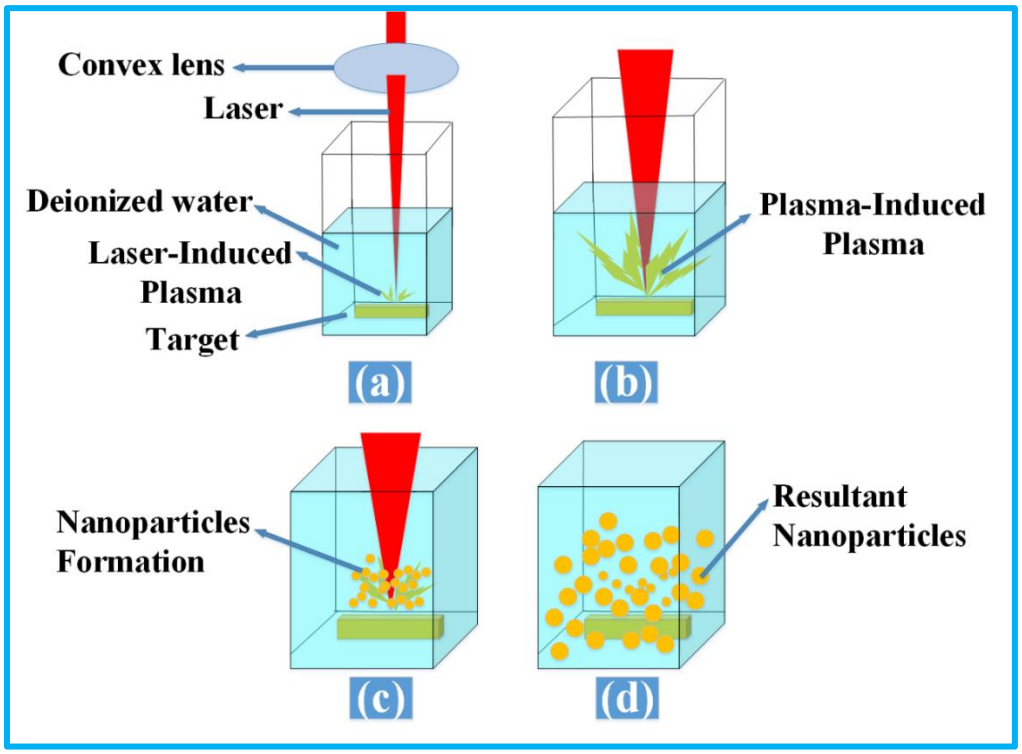

Figure 2. 4 Schematic mechanism of PLA evolution in liquid

Chemical processes within the plasma at high temperatures can generate the metastable phase in the first stage[110]. Reactant species from the target and liquid then start to interact and impact one another in the second set of reactions. In the third section, these produced reactant species interact with liquid-like molecules in high-temperature chemical reactions[110]. The process of pushing the ablated species into liquid by high pressure within the plasma-induced plasma is known as the fourth phase[110]. NPs start to form when these four different types of processes are finished, which involves cooling down and condensation in the confining liquid.

2.6.2 Chemical Bath Deposition of Nanoparticles (CBD-NPs)

Nanostructured materials have gained much interest over the last few decades, and one of the essential roles in developing these nanostructured materials-based applications is their synthesis process. A variety of techniques have already been developed to fabricate nanostructured materials. Among them, Chemical Bath

Deposition (CBD), sometimes called chemical solution deposition, is a low-cost simple deposition method by which films are "grown" on the substrate by a chemical reaction that occurs in an aqueous solution. In this procedure, the reaction between the cations and anions leads a layer of chemical compounds to grow on the substrate.

Additionally, in the bulk of the solution, a precipitate forms. The CBD-NPs method is another frequently employed process for depositing thin nanostructured films into nanoparticles (NPs) solutions. This alternative method of CBD-NPs also doesn't require sophisticated or expensive tools or equipment like the CBD technique because the necessary chemicals are easily obtained and reasonably priced[111]. The first time CBD was used to deposit silver thin film for the mirror objective was in 1835, reported by M. Aida and team[112], while the CBD-NPs technique has received tremendous interest for the last few decades. The fundamental idea underlying the fabrication of created thin films using the CBD-NPs technique is the low-temperature (below 100°C) controlled precipitation of intended thin films from a collided NPs solution. CBD-NPs have gained popularity among other deposition techniques because it is easy to implement, inexpensive, suitable for highly homogeneous layers on large-scale deposition areas[113], and prevent the oxidation of a variety of substrates[114], including metals, semiconductors, and insulators. It also makes it simple to control the properties of the thin film by adjusting the deposition parameters.

2.6.2(a) Principle of CBD-NPs Technique

Precipitate formation occurs during chemical (NPs) solution deposition when the reactant ionic product surpasses the solubility product at an approximately specified temperature (below 100°C). Partially soluble ionic nanoparticles (NPs) are soluble according to the solubility product. More ion products and solubility products are associated with more soluble NPs. However, the solubility product is also dependent on

the quantity of ions present[115]. The resulting solid phase will dissolve back into the solution if the ionic product is not higher than the solubility product, preventing precipitation. This is the underlying principle by which nanoparticles are deposited via chemical solution deposition.

2.6.2(b) Mechanism of Thin Film Deposition in CBD-NPs Technique

The deposition of the thin films via CBD-NPs happens through the following four mechanisms such as ion-by-ion, simple cluster, complex decomposition cluster, and complex decomposition ion-by-ion[116]. Anions are involved in basic ion-by-ion and basic cluster (hydroxide) processes. Conversely, the ion-by-ion and cluster mechanisms of complex breakdown entail the dissolution of carbon–chalcogen bonds[116]. Ionic reactions occur sequentially in this deposition method. The below relation is denoted as the response of the general mechanism[116],

$$M^{n+} + X^{m-} \longrightarrow M_mX_n \qquad (2.1)$$

Ionic product $[M^{n+}][X^{m-}]$ exceeds M_mX_n's solubility product, K_{sp}, to produce solid M_mX_n) [116]. Thus, in the event that the ionic product is less than the solubility product, K_{sp}, no solid phase will separate. Precipitation is an equilibrium process rather than a one-way process as a result. Hodes et al. state that to keep metal ions in the solution and stop hydroxide from precipitating out, an appropriate complexing agent is added to the aqueous solution[116].

A variety of factors affect the development of films when CBD-NPs are used. The pH level of the solution, the reaction of the bath's temperature, the types and concentrations of reactants, the type and concentration of the complexing agent, the distances between the substrates, and the length of the reaction are among them. Each of these variables has no independent influence on the chemical reaction; rather, the

outcome is the product of the interaction of all these variables[117]. In the reaction bath, different circumstances yield different film characteristics.

2.7 Nonlinear Optics (NLO) Studies

A phenomenon known as Nonlinear Optics (NLO) appears when sufficiently intense light interacts with different materials to produce new optical properties including an amplitude, phase, and frequency alteration of the electromagnetic field. Both organic and inorganic materials exhibiting nonlinear optical (NLO) effects are currently one of the major focuses of researchers. In particular, the Second Harmonic Generation (SHG), and the Third Harmonic Generation (THG), which are simply the doubling and tripling of the frequency of incident light, respectively, are one of these phenomena[118, 119]. Depending on the variety of materials leveraged to investigate nonlinear phenomena, nonlinear optics has fragmented into numerous fields. Significant technological impacts result from the capacity to control the frequency of light, phase, polarization, or light path. The speed at which related fields like photonics, computers, optical signal processing devices, optical data storage, dynamic image processing, fibre optics, and optical communications have advanced technologically has an immediate impact on the expansion of nonlinear optics research.

2.7.1 Origin of NLO

John Kerr, a 19^{th}-century experimentalist, is frequently acknowledged as the pioneer of Nonlinear Optics (NLO), who observed the optical second harmonic generation for the very first time in 1961[120]. The study of NLO aims to comprehend the behaviour of light-matter interactions in situations where the applied electromagnetic field has a nonlinear effect on the material. An intense beam propagating through a material may cause NLO effects to occur. The charged particles

in the medium oscillate around their equilibrium positions when an electromagnetic wave travels through the material, even in the linear regime. The effectiveness of the second-order and third-order phenomena is described by the magnitude of $\chi^{(2)}$ and $\chi^{(3)}$, respectively. Although they are extremely difficult to identify and have minimal significance on materials, higher-order words are also accessible.

2.7.2 Measurement Methods

A variety of methods has evaluated the NLO properties of materials, the most widely used being Z-scan, optical Kerr-gate, pump-probe measurements, hyper-Rayleigh scattering, degenerate four-wave mixing (DFWM), second and third harmonic generation (Sutherland, 1996). In this study, I have employed the Z-scan method among other measurement techniques. The Z-scan investigation is a sensitive single-beam technique that identifies the far field sample transmittance as a function of sample position and is used to quantify the optical nonlinearity of the crystal by moving the sample through the Gaussian beam's focus[121]. In 1990, this straightforward and widely used experimental technique was developed by Sheik-Bahae et al.[122]. The schematic diagram of a Z-scan experimental setup is portrayed in Figure 2. 5.

Here, molecule excitation is achieved using a Gaussian laser beam, with the Z-axis serving as the beam's propagation direction. With a convex lens, the beam is focused, and Z=0 is assumed to be the focal point. For both positive and negative values of Z, the beam's energy density undoubtedly reaches its maximum at the focus and symmetrically decreases towards either side of it. To conduct the experiment, the sample is positioned in the beam at various angles to the focus (different values of Z), and the corresponding transmission is measured. Thus, the specimen experiences various laser intensities at each position, and the obtained position-dependent