Synthesis of photoluminescent carbon dots and their application in security ink development

A thesis submitted towards partial fulfilment of the requirements for the degree of:

Master of Technology in Nano Science and Technology

Submitted by:

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CERTIFICATE OF RECOMMENDATION

This is in order to certify that the thesis entitled "Synthesis of photoluminescent carbon dots and their application in security ink development" is a legitimate work done by Soudip Mitra under our supervision and guidance for the purposes of fulfilling the requirement for the degree of Master of Technology in Nano Science and Nanotechnology in the School of Materials Science and Nanotechnology from the academic session 2021-2023.

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I hereby endorse the foregoing thesis as an engineering study, conducted and presented in a manner satisfactory enough to justify its acceptance as an engineering study, in order to obtain the degree for which it has been submitted. This approval does not endorse or approve any statement made, opinion expressed or conclusion drawn therein, but merely approves the thesis for the purpose for which it has been submitted.

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I hereby declare that this thesis contains a literature survey and original research work by the undersigned candidate for the Master of Technology (Nano Science and Technology) program during the academic year 2021-2023.

The information in this document has been gathered and presented according to academic standards and ethical conduct.

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ABSTRACT

The study mentioned in the thesis "Synthesis of photoluminescent carbon dots and their application in security ink development" primarily involves two concerns: first, the synthesis of Carbon Dots, and second, the preparation of stable fluorescent ink.

Carbon dots (CDs), which are generally small carbon nanoparticles (less than 10 nm in size) with various unique properties, have found wide use in more and more fields during the last few years. Moreover, CDs are environmentally beneficial due to their non-toxic and inert qualities, which have enhanced the interest of academic and industrial researchers alike. The primary objective is to synthesize Carbon Dots using hydrothermal and microwave synthesis processes. Their structural and optical properties have been researched and characterized. The control of its size and form was achieved by adjusting the time and temperature in the preparation parameter. CDs have been thoroughly discussed in all areas, including their prospective uses in fluorescent ink development. The diverse application of Carbon Dots are discussed in this course of work.

Chapter 1

Introduction

1.1 Nanostructures

Nanostructured materials [1-4] are of interest because they can bridge the gap between the bulk and molecular levels, generating new applications, especially in electronics, optics & optoelectronics, and biological sciences. When a material demonstrates a distinct variation of optical and electronic properties with a particle size variation of 100 nm, it is referred to as a nanostructure, and it is classified as

1. two-dimensional, e.g., thin films or quantum wells,
2. one-dimensional, e.g., quantum wires
3. zero-dimensional or dots.

1.2 Carbon

Carbon is an exceptional material that is abundantly found in Earth in the form of coal, and it is one of the causes of the existence of life on this planet. It has lately astonished us once more in the form of carbon quantum dot [5].

As shown in Fig. 1, graphitic forms of carbon include zero-dimension (0D), one-dimension (1D), two-dimension (2D), and three-dimension (3D) graphite.

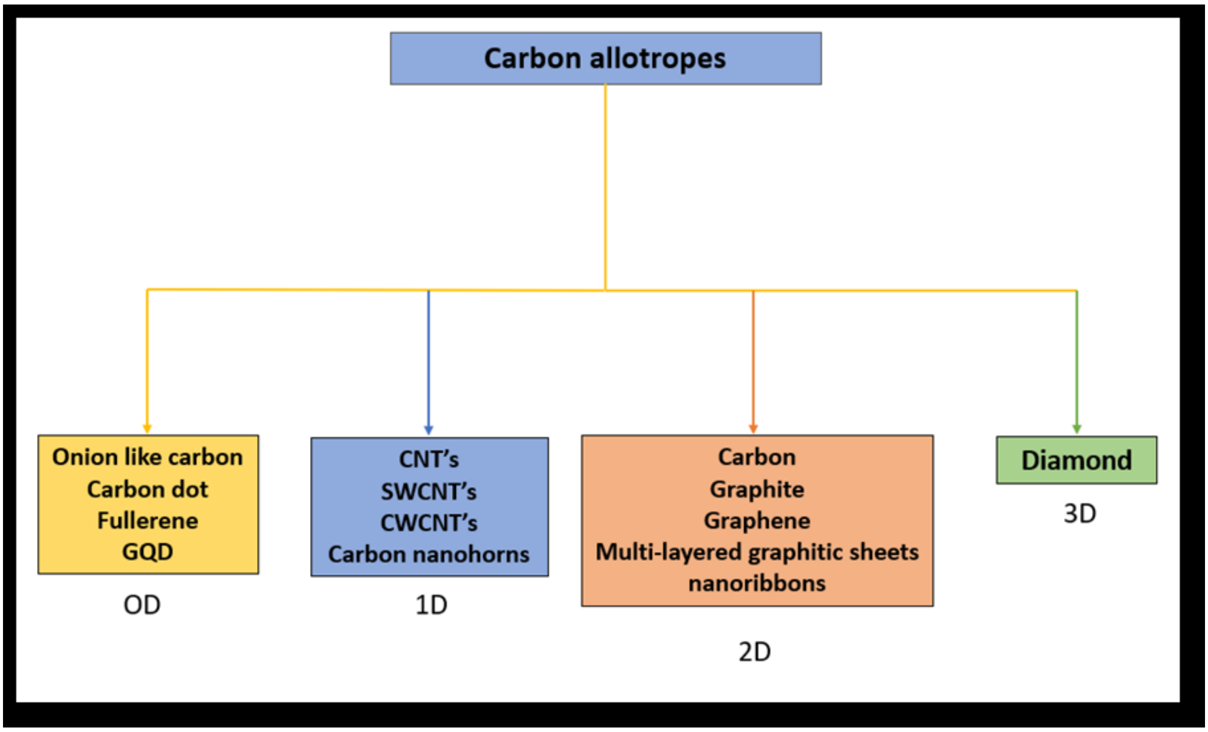

FIGURE1.1: Classification of Carbon materials

1.3 Quantum Dots

Quantum dots (QD) are man-made nanoscale semiconductor structures composed of elements from groups II to VI or III to V. They are described as particles with physical dimensions smaller than the exciton Bohr radius. When exposed to UV light, these semiconducting nanoparticles can emit a range of colours. These nanoparticles of synthetic semiconductors are employed in composites, energy harvesting, and fluorescent biological imaging [14,15]. Many basic features in the nano range are size dependent, therefore focus has been given to the optoelectronic properties of nanostructured semiconductors or quantum dots over the last few years.

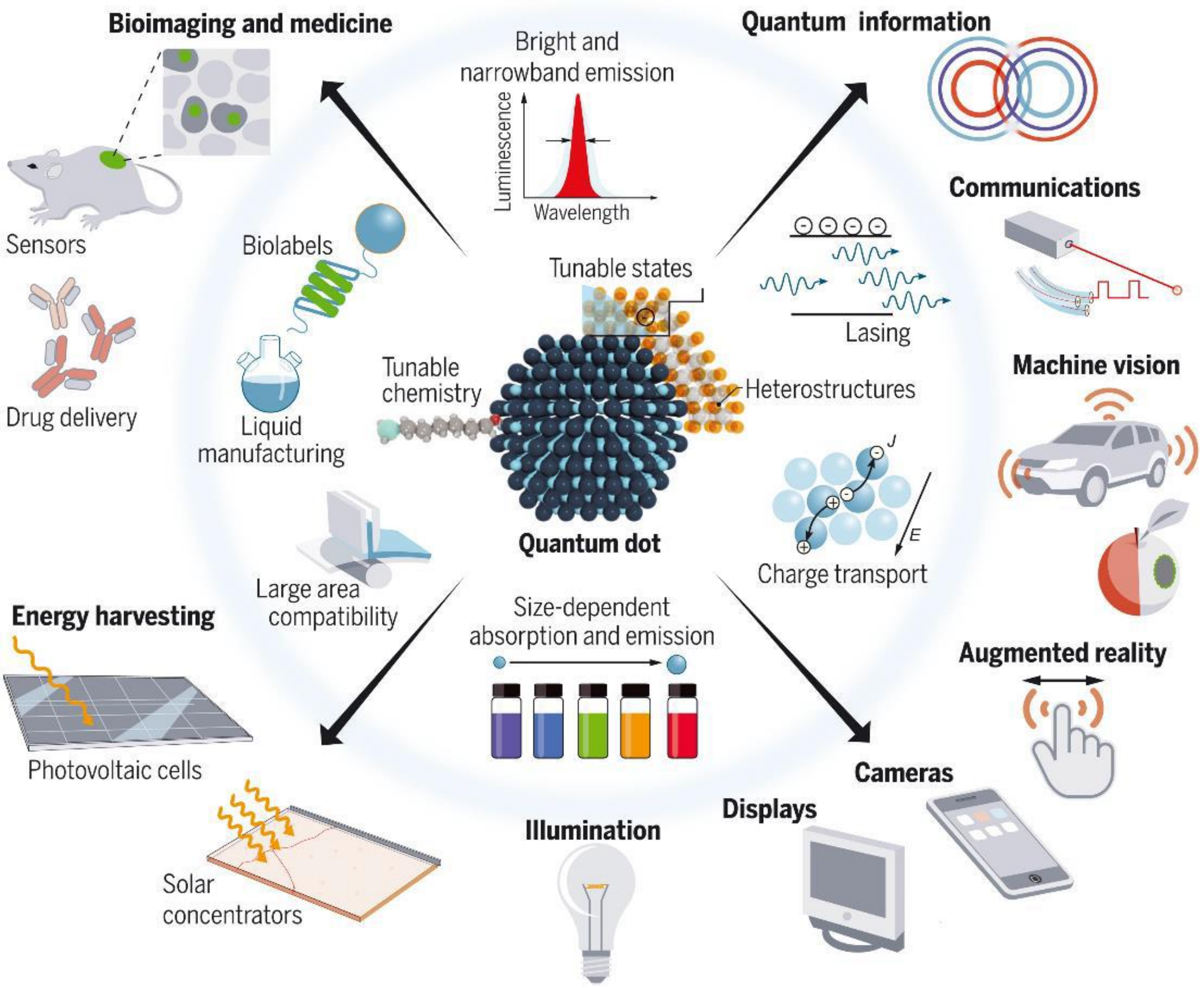

FIGURE 1.2: Applications of CQDs

1.3.1 Carbon Dots and types

Carbon dots (CDs) are a broad term for a variety of carbon materials such as carbon quantum dots (CQDs), graphene quantum dots (GQDs), carbon nanodots (CNDs), and carbonized polymer dots (CPDs). These CDs family members are characterized according to their own characteristics, surface groups, and carbon core structures [16,17].

1.3.2 Doping of Carbon Dots

The size of Carbon dots is typically controlled by the concentration of reactants, reaction temperature, duration, surfactants, additives, etc. The microwave approach, for example, was utilized to create extremely luminous Carbon dots from a wide range of precursors. Until now, the bulk of studies has reported the production of blue-emitting Carbon dots with excitation-dependent emission spectra. Furthermore, the emission spectra of Carbon dots can be modified by doping with elements such as nitrogen (N), sulphur (S), phosphorus (P), boron (B), or mixtures of these elements [22-26]. It has been demonstrated that doping Carbon dots increases fluorescence and shifts emission spectra. Fluorescent Carbon dots with green emission spectra, for example, have been reported and used for sensing and cell imaging [27]. Carbon dot's electronic structures can be altered by inserting atomic impurities, resulting in n-type or p-type carriers. As a result, by applying different types and amounts of doping atoms, their optical and electrical properties can be modified.

1.3.3 Properties of Carbon Dots

1.3.3.1 Fluorescence

In fluorescence, the singlet spin state S_0 is the ground state of the electrons, and S_1 and S_2 are singlet excited states. Within those states, there are several energy levels. The higher the level is, the more energy an electron possesses when being in that level. In the case of singlet states, the electrons have antiparallel spins. The electrons are lifted from the ground state S_0, for example, to an energy level of the second excited state S_2, when excited by electromagnetic radiation. After excitation stops, the electrons only stay in that excited state for a short period of time and then immediately start falling back down into the ground state. In doing so, energy initially can be released to the surroundings by vibrational relaxation. That means thermal energy is released by the motion of the atom or molecule until the lowest level of the second excited state is reached. The bigger gap between the second and first excited state is overcome by internal conversion. That describes an electronic transition between two states while the spin of electrons is maintained. Now, the electrons can relax further due to more vibrational relaxation until they reach the lowest energy level of the S_1 state. Theoretically, the electrons could relax even further in a non-radiative way until they eventually reach the ground state again. However, it can be the case that the last amount of energy is too large to be released to the surroundings because the surrounding molecules cannot absorb this much energy. Then, fluorescence occurs, which leads to an emission of photons possessing a certain wavelength. The emission lasts only until the electrons are back in the ground state. Since during all those transitions the electron spin is kept the same, they are described as spin-allowed.

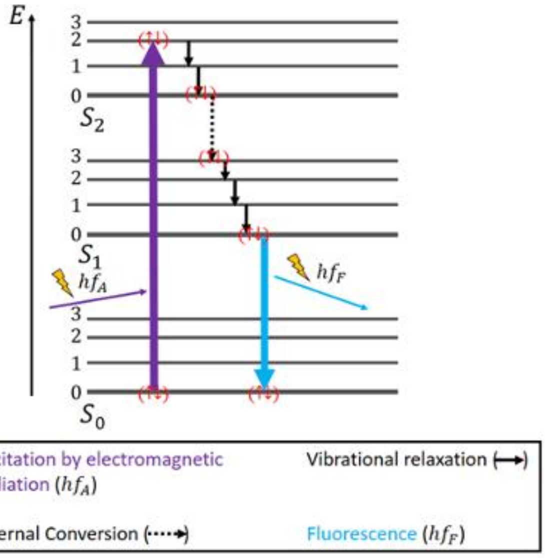

FIGURE 1.3: Mechanism of Luminescence

1.3.3.2 Phosphorescence

For phosphorescence, things are a bit different. There are again an S_0 ground state and the two excited states, S_1 and S_2. Additionally, there is an excited triplet T_1 state which lies energetically between the S_0 and S_1 state. The electrons again have antiparallel spins in the ground state. Excitation happens in the same way as in fluorescence, namely through electromagnetic radiation. The release of energy through vibrational relaxation and internal conversion while maintaining the same spin is the same here, as well, but only until the S_1 state is reached. Alongside the singlet states, a triplet state exists and so-called intersystem crossing (ISC) can occur since the T_1 state is energetically more favorable than the S_1 state. This crossing, like internal conversion, is an electronic transition between two excited states. But contrary to internal conversion, ISC is associated with a spin reversal from singlet to triplet. Electrons in the triplet state have parallel spins, which is noted as (↑↑). This ISC process is described as “spin-forbidden”. It is not completely impossible – due to a phenomenon called “spin-orbit coupling” – however, it is rather unlikely. In the T_1 state, non-radiative decay is possible as well. However, a transition between the lowest energy level of the triplet state and the S_0 state is not readily possible, because that transition is spin-forbidden, too. Still, it can happen anyway with a small possibility. It causes a rather weak emission of photons because the electron spin has to be reversed again. The energy is trapped in this state for a while and can only be released slowly. After all energy has been released, the electrons are back in the ground state.

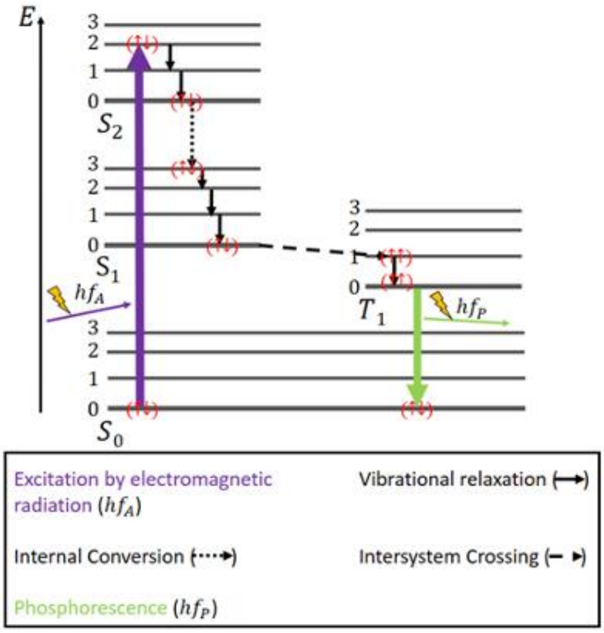

FIGURE 1.4: Mechanism of Phosphorescence

1.3.3.3 Chemiluminescence

Chemiluminescence (CL) is the luminescence produced by chemical reactions that induce the transition of an electron from its ground state to an excited electronic state. When the excited molecule decays to the electronic ground state, CL emission at different wavelengths occurs, from ultraviolet-visible to infrared radiation.

1.3.3.4 Electrochemical luminescence

Electrochemical luminescence (ECL) is the process where species generated at electrodes undergo electron transfer reactions to form excited states that emit light. Application of a voltage to an electrode in the presence of an organic or inorganic luminophore results in light emission.

1.3.3.5 Up Conversion Luminescence

Upconversion luminescence is an optical process that emits high-energy photons by absorbing two or more low-energy photons, which is caused by anti-Stokes luminescence, has attracted significant attention in recent years. Upconversion nanomaterials are superior to quantum dots and organic dyes because of their unique properties, including non-photobleaching, non-blinking, low-toxicity, photostability, high conversion efficiency, high light penetration in biological tissues and long lifetime, from nanoseconds up to 6 orders of magnitude to milliseconds, which render them an ideal kind of fluorescent labels for a variety of analytical formats as well as bioimaging in cancer therapy, showing great potential for both in vitro and vivo imaging and biodetection assays applications.

1.3.3.6 Photo Induced Electron transfer property

Photo induced electron transfer (PET) between organic fluorophores and suitable electron donating moieties, for example, the amino acid tryptophan or the nucleobase guanine, can quench fluorescence upon van der Waals contact and thus report on molecular contact. PET-quenching has been used as reporter for monitoring conformational dynamics in polypeptides, proteins, and oligonucleotides. Whereas dynamic quenching transiently influences quantum yield and fluorescence lifetime of the fluorophore, static quenching in π-stacked complexes efficiently suppresses fluorescence emission over time scales longer than the fluorescence lifetime. Static quenching therefore provides sufficient contrast to be observed at the single-molecule level [28].

1.4 Applications

Sensors: CQDs can act as good sensing materials due to their high electron mobility and fast reactivity, making them excellent candidates for sensing applications. CQDs have previously been investigated for applications such as field-effect transistors, photovoltaic, light-emitting diodes, electrochemical sensors, glucose sensors, PL sensors, ECL sensors, bioimaging, and bio-labelling

Bio-medical: CQDs are used in bio-imaging, bio-sensing, and drug delivery systems.

Energy: Quantum dots have applications in energy storage as supercapacitors and lithium-ion batteries, as well as energy conversion as solar cells.

Catalytic: CQDs have high catalytic activity and are widely used as a catalyst in processes such as photocatalytic hydrogen evolution and CO2 reduction, electrocatalytic oxygen reduction, water splitting and CO2 reduction, and photoelectron catalysis.

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CHAPTER 2

NANOTECHNOLOGY

&

NANOMATERIALS

2.1 Introduction

The prefix 'nano' refers to a Greek prefix that means 'dwarf' or very small and represents one thousand millionths of a metre (10-9 m). We must differentiate between nanoscience and nanotechnology. Nanoscience is the study of structures and chemicals on nanometer scales ranging from 1 to 100 nm, and nanotechnology is the technology that uses in practical applications such as devices [1]. In comparison, a single human hair is 60,000 nm thick and the DNA double helix has a radius of 1 nm (Figure 1) [2].

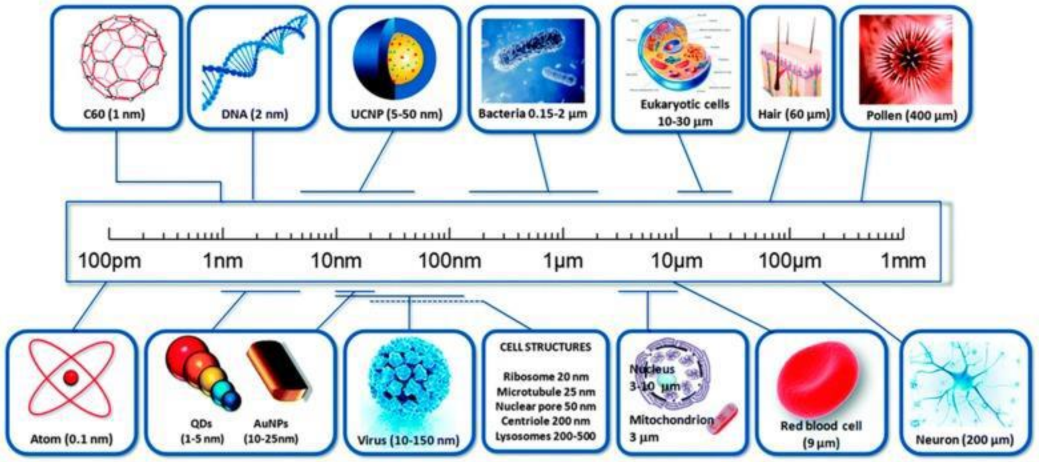

FIGURE 2.1: A comparison of sizes of nanomaterial

Nanotechnology is one of the most promising 21st-century technologies. It is the ability to apply nanoscience theory by viewing, measuring, manipulating, assembling, regulating, and creating materials on a nanoscale scale. Nanotechnology is defined by the National Nanotechnology Initiative (NNI) in the United States as "a science, engineering, and technology conducted at the nanoscale (1 to 100 nm), where unique phenomena enable novel applications in a wide range of fields, from chemistry, physics, and biology, to medicine, engineering, and electronics."

Nanoscience is the application of physics, materials science, and biology to the manipulation of materials at the atomic and molecular levels, whereas nanotechnology is the ability to observe, detect, modify, construct, regulate, and manufacture matter at the nanometer scale [3].

2.2 Properties of Nanomaterial

1. Dimension: at least one dimension ranging from 1 to 100 nanometres (nm).

2. Methodology: developed with approaches that demonstrate fundamental control over the physical and chemical properties of molecular-scale formations.

3. Building block property: They can be merged to construct larger structures. In general, nanoscience is relatively natural in microbiological sciences because the sizes of many bioparticles dealt with (such as enzymes, viruses, and so on) fall within the nanometer range.

4. Large area/volume ratio: The surface area/volume ratio has a greater impact on certain properties of nanoparticles than on bulk particles.

5. Interfacial layer: The interfacial layer created by ions and molecules from the medium that are within a few atomic diameters of the surface of each particle for nanoparticles dispersed in a medium of diverse compositions can conceal or change its chemical and physical properties. That layer is, in fact, an essential component of each nanoparticle.

2.3 Applications of Nanotechnology

Nanotechnology is being applied in a wide range of scientific domains, with a wide range of unique applications. When a particle is shrunk to the nanoscale, the properties of the substance change proportionally to its size. As a result, it creates new opportunities in a range of industries. There is greater surface area to react when the surface-to-volume ratio grows with size. The diameter or size of particles influences a variety of optical and mechanical qualities.

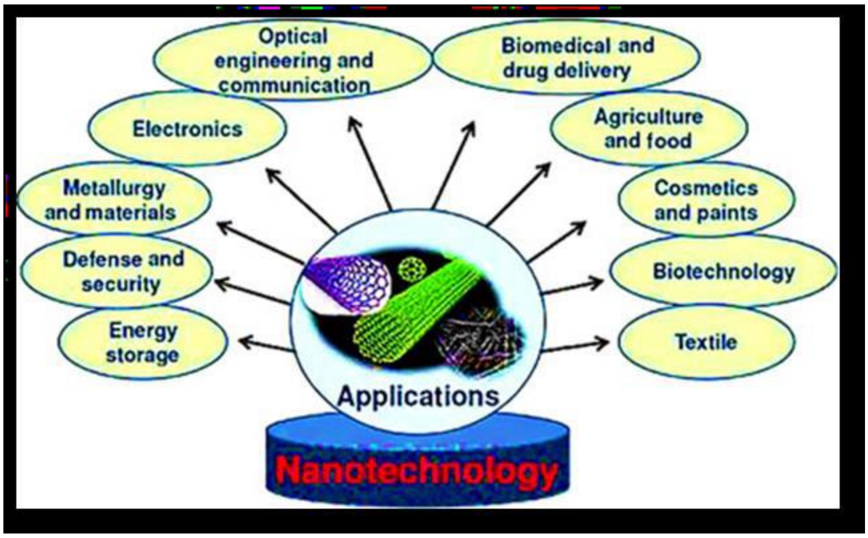

FIGURE 2.2: Applications of Nanotechnology

1. **Electronics:** In electronics, nanotechnology allows for faster, smaller, and more portable systems. Nanoelectronics improves electrical device capabilities, boosts memory chip density, and reduces power consumption and transistor size in integrated circuits.

2. **Energy storage:** Nanotechnologies, such as novel ceramic, heat-resistant, and still flexible separators and high-performance electrode materials, can significantly improve the capacity and safety of lithium-ion batteries [4].

3. **Biomedical and drug delivery:** Nanotechnology applications in several biology-related domains, such as diagnosis, medicinal delivery, and molecular imaging, are being extensively explored and yield promising results. In the realm of nano-oncology, remarkable progress has been made in enhancing the efficacy of standard chemotherapeutic medications for a variety of aggressive human tumours [5,6].

4. **Defence and security:** Nanomaterials have the potential to make firearms lighter and with more ammunition. When these new technologies are combined, they may lead to guns that can automatically target and fire self-guided rounds if an attacker is identified. Nanorobots are capable of attacking and destroying weaponry, metals, and other objects [7].

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7. Nanotechnology for Defense and Security Christian Ngo & Marcel H. Van de Voorde

Chapter 3

SECURITY INK

3.1 Security Inks

Counterfeiting or forgery is a universal issue that poses a threat to an individual as well as society. It could create significant negative impacts on the public, and even deteriorate the economic growth through the circulation of illegal or fake goods, documents and currency. Another serious risk is the counterfeits of medicinal products in the drug market that could harm public health and safety, as the manufactures can evade quality checks and certification. Hence, there are serious environmental, health, economic, and social effects that counterfeiting leaves in its wake, and these accelerated growths of forgeries challenge researchers globally to come up with innovative and extremely secure anti-counterfeiting techniques to combat the issue. The development of materials that can offer smart features in creating non-forgeable security codes and markers are presently a thrust area of research to provide a safe and sustainable environment for consumers and businesses. In recent years, diverse anti-counterfeiting, verification and authentication technologies have been developed to safeguard documents and products such as signature-DNA-marker packaging materials, magnetic response plasmonic security labels, anti-theft tags and RFID (Radio-Frequency Identification) based smart labels and luminescence printing. However, some of these approaches are cloneable owing to predictable and deterministic encoding mechanisms. Amongst these different strategies, luminescence printing is widely used against counterfeiting as it offers several advantages such as the facile design of luminescent materials, easy handling and high-throughput. In order to develop suitable and unbreakable security printing features, appropriate material selection is extremely crucial and should follow specific fundamental characteristics such as easy synthesis with good yields, eco-friendly, stable for a long duration, cost-effective and most importantly, the features should be easy to identify but difficult to reproduce. In this context, luminescent materials have been in the forefront for its use in anti-counterfeits for optical data recording, storage and security. The optical properties featured by these materials are hard to copy. Hence, different categories of photoluminescent materials such as organic dyes, lanthanide-doped nanomaterials, carbon dots, quantum dots, metal-organic frameworks etc. are widely explored for security printing applications. Security inks help ensure the integrity of items needing high privacy and confidentiality, such as checks, documents, banknotes, certificates, passports, labels, and identity cards. Security inks support fraud detection and authentication. Security printing reduces the risk of forgery, tampering, or counterfeiting. Several technical methods are used in the security printing industry. Security printing is most often done on security paper, but it can also occur on plastic materials. Security inks are available to protect printed materials in different guises. The ink is invisible to the eye (covert) under normal lighting conditions. When passed under an ultraviolet lamp, the ink glows. This application is used predominantly for check printing and document protection.

3.2 Uses of Security Ink

A major factor driving the growth of the global security ink market is the increasing occurrences of forgery and counterfeiting practices.

Banknotes, identity cards, postage stamps, stock certificates, passports, and product authentication all see escalating counterfeiting. Efforts to reduce fraud costs are driving demand for security inks, expected to average annual growth of about 6% over the next several years.

Brand protection is another field where security ink is gaining importance. Brand protection against diversion, fraudulent claims, retail theft, and counterfeiting is a challenge. Security ink helps overcome such challenges, which is another driving factor for the growth of the global security ink market.

From lost revenue, consumer safety, homeland security, and brand integrity, businesses fight a continuing battle against counterfeiters. The cost of counterfeit products in the United States alone totals $600 billion.

3.3 Types of Security Ink

There are several different types of security inks, all of which effectively protect against counterfeiting methods. The inks most commonly used for security printing include

3.3.1 Invisible Ultraviolet Ink

The most common security ink is invisible to the naked eye. The latent image appears when placed under a UV lamp. Most often used for printing currency and labels.

3.3.2 Visible Fluorescent Ink

One or more fluorescent inks can be combined or used with traditional inks. Fraudulent products and documents may appear the same until the legitimate printing with visible fluorescent inks is exposed to UV light, making it glow.

3.3.3 Infrared Invisible Ink

IR invisible inks remain completely invisible to the eye yet can be seen using modified photo and video equipment that responds to colors in the infrared spectrum. These inks do not fluoresce in the visible range and cannot be seen with ultraviolet lights.

3.3.4 Taggant Inks

Taggant ink formulations contain unique chemistry paired with a detector for identifying the signature. The combination creates a lock and key relationship. These anti-counterfeit inks can be used on security labels or printed directly onto product packaging. Taggant ink is well suited to be printed on various substrates, including anti-counterfeit labels and more.

3.3.5 MICR

Magnetic Ink Character Recognition (MICR), streamlines check processing for financial institutions. The characters are printed with special MICR fonts with MICR ink that contains a percentage of fine metallic pigment. It is the combination of ink and fonts that create the machine-readable text and numbers. Fraudulent documents printing without MICR ink would be immediately rejected, even at a point of sale.

3.4 Carbon Dots in Security Ink Application

Recent years have perceived the development of a diverse assortment of luminescent nanoparticles for security printing applications [5]. Carbon dots (CDs) are a fascinating class of zero-dimension carbon nanoparticles belonging to the nanocarbon family with generally less than 10 nm size, but can be as small as even 1 nm and as large as 60 nm. The presence of multiple functional groups, fascinating optical features with unique chemical and photostability, along with excellent biocompatibility of CDs attracted the attention of material scientists. After a comprehensive study on several interesting research reports, the fluorescent carbon dots (CDs) are classified as Carbon Nanodots (CNDs), Carbon Quantum Dots (CQDs), Graphene Quantum Dots (GQDs) and Carbonized Polymer Dots (CPDs) mainly based on their nature, crystalline structure and quantum confinement. Fluorescent CDs are the most stable allotropes of carbon, with unique electronic and optical properties. They have always been popular amongst researchers due to their extensive applications in diverse areas including bioimaging, photocatalysis, sensing, lasers, LEDs, gene transmission, drug carriers and energy conversion/storage devices.

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Chapter 4

Research Methodology

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Literature Review

4.1 Synthesis routes of carbon dots

The various routes have been proposed to fabricate the CDs with desired properties for a particular application during the last decade. Generally, these well-established synthesis strategies of CDs are classified into “top-down” and “bottom-up”. The top-down strategies include ultrasonic synthesis, chemical exfoliation, electrochemical oxidation, arc-discharge, and laser ablation. In general, GQDs, 2D nanoparticles, are obtained by “top-down” strategy from the exfoliation and cutting of macroscopic carbon structures with the obvious graphene lattices, such as graphite powder, carbon black, activated carbon, carbon nanotubes, carbon soot, and carbon fibers.

Top-down approaches generally require long processing times, harsh reaction conditions and expensive materials and equipment. This strategy is suitable for mass production. In contrast, CQDs and CPDs, both are 3D nanoparticles with spherical core, are typically synthesized from the bottom-up approaches. The CQDs and CPDs are produced via polymerization of molecular precursors, such as glucose, sucrose, and citric acid, through microwave pyrolysis, solvothermal reactions, plasma treatment and chemical vapor deposition, which show fewer defects and high controllability. Here, we will elaborate the main methods for CDs synthesis, size control and surface moieties by treatment of confined pyrolysis and modification. Surface properties of CDs could be optimized during preparation or further treatment for the selected applications.

4.1.1 Top-Down Approach

1. Chemical Exfoliation

Chemical exfoliation is a facile and convenient method for mass production of high-quality CDs without complicated devices. The precursor carbon materials (carbon fibers, graphene oxide, carbon nanotubes) are cleaved by strong acids or oxidizing agents. However, it is a tedious process to further purify the product by the removal of excess H_2SO_4, increasing the overall synthesis cost.

2. Laser Ablation

As a unique and promising synthesis route, laser ablation has been applied in the preparation of CDs owning to advantages of short period and simple operation. CDs with visible, stable and tunable PL performance were synthesized by laser rapid passivation of carbon particles, and demonstrated that passivation by laser irradiation has an important influence on the origin of PL.

3. Ultrasonic Assisted Treatment

It is acknowledged that ultrasonic-assisted method has the advantages of low cost and simple operation for the preparation of CDs. Alternate high-pressure waves and low-pressure were generated in the ultrasound process, which results in the formation and collapse of small bubbles in liquid. Thus, macroscopic carbon materials were cut into nanoscale CDs by strong hydrodynamic shear forces derived from the cavitation of small bubbles. Generally, researchers prepared the CDs with different properties by simply adjusting the ultrasonic power, reaction time and the ratio of carbon sources and solvents.

4.1.2 Bottom-Up Approach

1. Microwave Assisted Synthesis

A green, cost-effective microwave assisted strategy is widely employed to synthesize the CDs in less time. The obtained CQDs show good biocompatibility and low cytotoxicity. Microwave-assisted synthesis works on the basis of aligning dipoles of the material in an external field via the excitation produced by microwave electromagnetic radiations and is usually executed in combination with a known synthesis strategy. The process of alignment or orientation of molecules by the external electrical field may result in the production of internal heat which is responsible for a reduction in processing time and energy required. It is especially due to the heating homogeneity of microwaves. The reaction time can be fairly reduced by adopting microwave-assisted synthesis process.

2. Hydrothermal Synthesis

Hydrothermal strategy for the preparation of CDs has advantages of low cost and nontoxicity. Compared to other synthetic routes, hydrothermal method is a simple approach to synthesize CQDs. In general, the water solution of mixtures was enclosed with Teflon in an oven and hydrothermally reacted at high pressure and high temperature. Hydrothermal synthesis a unique method for crystallizing substances from high-temperature aqueous solutions at high vapor pressures; also termed “hydrothermal method." The term “hydrothermal” is of geologic origin.

Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave, in which a nutrient is supplied along with water. A temperature gradient is maintained between the opposite ends of the growth chamber. At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal.

3. Pyrolysis/Carbonization

Pyrolysis is a powerful technique to fabricate the fluorescent CDs by using macroscopic carbon structures as precursors in recent years. This method offers advantages of short reaction time, low cost, easy operation, solvent-free approaches and scalable production. The four main processes including heating, dehydration, degradation and carbonization are critical factors for conversion of the organic carbon-containing substance into CQDs under high temperature. Carbon precursors are cleaved into carbon nanoparticles by using high-concentration alkali or acid in the pyrolysis process.

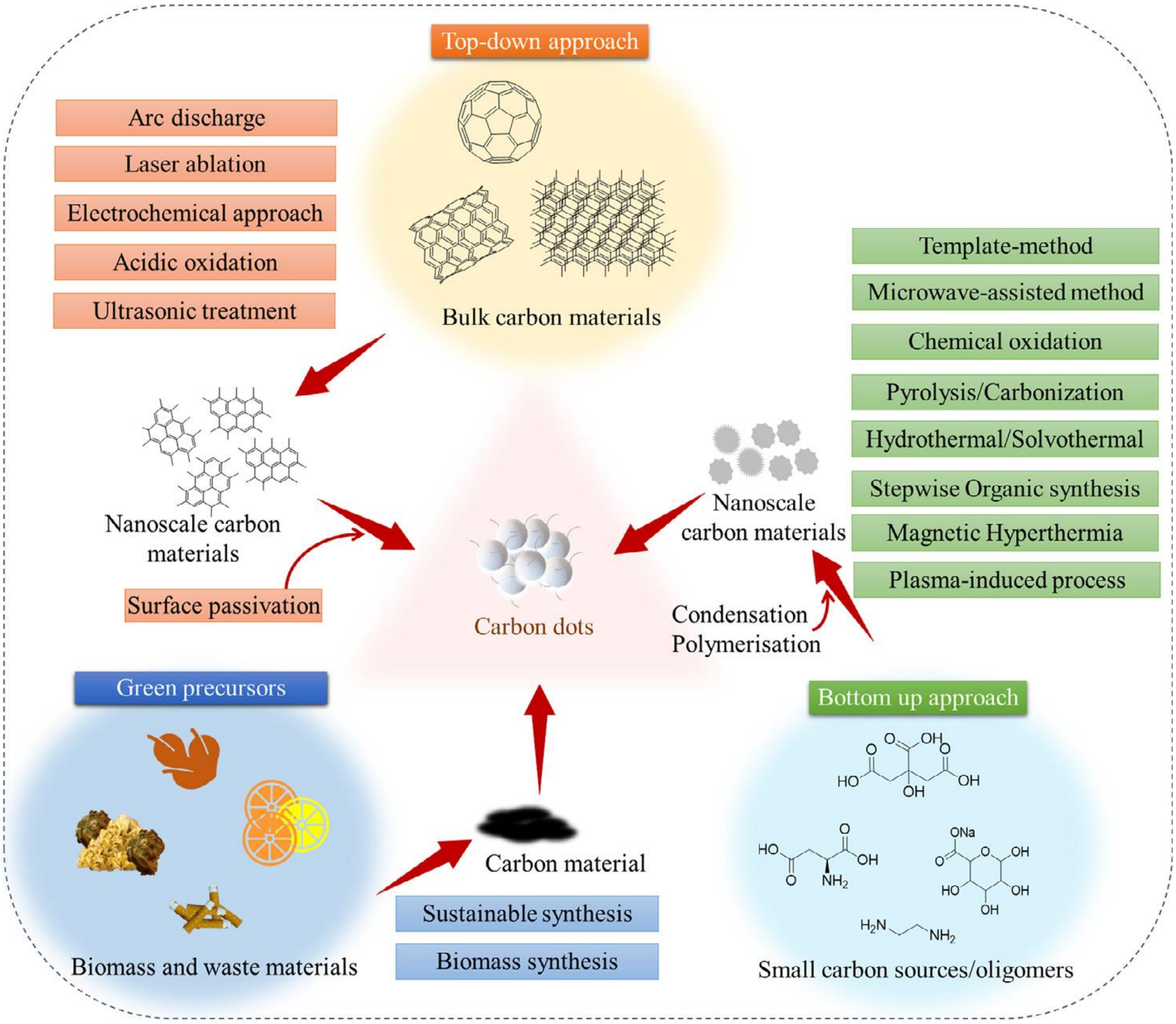

FIGURE 4.1: Synthesis Routes of Carbon Dots

4.2 Origin of Luminescence of Carbon Dots

Fluorescent CDs prepared from various synthetic precursors, and subsequently through different methods and post-treatments exhibit diverse optical performances, demonstrating an intricate system. Hence a unified theory cannot be formulated for the origin of fluorescence. The fluorescence in CDs originates due to mainly four mechanisms: (i) perfect carbon crystals with fewer defects, and core-state emission induced by modified functionalities (ii) the hybridisation of the carbon backbone, degree of surface oxidation and connected chemical functional groups deter- mining the surface state emission quantum confinement effect influences the fluorescence from bandgap transitions of con- jugated π-domains and size-dependant energy relaxation dynamics, and (iv) fluorescent impurities and the by-products generated during the preparation of CDs. However, in spite of the diversity in the structures, CDs possess a few similar absorptions and emission properties, which are summarised: a typical strong absorption at 230–360 nm in the UV range: for the carbon core, an absorption maxima (λmax) at 230–265 nm (π–$\pi*$transition, aromatic C = C bonds), λmax at 300 nm (n–$\pi*$transition, C = O bonds), λmax at 355–360 nm (n–$\pi*$transition, C-N/C = N bonds) etc., with a tail extending into the visible region. The excitation-independent fluorescence features related to the lower wavelength region could be due to the presence of heteroatoms or doping

4.3 Emission Features of Carbon Dots

The emission properties of fluorescent CDs may reflect not only the effects from varying particle sizes within the sample, but also the distribution of different emissive points of each CD. Another feature of CDs is their fascinating tunable PL that arises from quantum confinement. Most fluorescent CDs emit blue and green under UV light and demonstrate excitation wavelength-dependant emission (red-shift with increasing excitation wavelength). The broad nature of the emission spectra observed in fluorescent CDs is attributed to the considerable heterogeneity (both in chemical composition and size), resulting from poorly controllable synthesis processes.

4.4 Photostability of Carbon Dots

Photostability refers to stable fluorescence emission intensity after prolonged and continuous excitation. Fluorescent CDs usually display excellent photostability due to their large π-conjugated structural framework. Moreover, after surface passivation they typically show nonblinking PL. Fluorescent CDs have good photostability and are nonblinking at the single-particle level. In contrast, fluorinated CQDs show good photostability, which could be due to reduced electron density of the aromatic structure appended with highly electron-withdrawing fluorine.

4.5 Literature Review

Ref.No	Ink name	Stability	Synthesis Method	Excitation Wavelength	Emission Colour
1	ZnO QD ink	High stability	Sol Gel method	365nm	Red fluorescence
2	LuVO4:Eu ink	Lifetime of 0.934ms	Microwave Irradiation method	312nm	Strong Red fluorescence
3	Hydroxypatite NP	pH, doping dependent stability	Hydrothermal method	244nm	Strong Red fluorescence

4	Eu3+ doped CazrO3	High structural stability	Microwave assisted hydrothermal method	250nm,350nm	Red fluorescence
5	Terbium doped BaWO4	Excellent stability	Hydrothermal Method	230nm, 340nm	Dual green and bluish emission
6	YVO4:Eu3+ doped ink	Average lifetime 0.62ms	Microwave method	270nm	Red emission
7	Boron doped CD	Good photochemical stability	Hydrothermal method	365nm	Blue emission
8	Carbon Nitride QD	Excellent photostability	Hydrothermal method	378nm	Bright blue emission
9	N/S-CD ink	High photostability	Hydrothermal method	360nm	Strong green emission
10	Carbon dot invisible ink	Highly photostable	Microwave method	330nm	Strong blue emission
11	N-CD ink	High optical stability	Hydrothermal method	356nm	Blue fluorescence
12	N/P-CQDs	Stability dependent on pH	Hydrothermal method	380nm	Blue fluorescence
13	N-CQD inks	Strong fluorescence stability	Hydrothermal method	370nm	Strong blue fluorescence

14	F/N-GQD ink	Superior photostability for long time	Hydrothermal method	390nm	Bright green fluorescence
15	GQD ink	Stability for more than a year	Hydrothermal method	265nm, 340nm	Pure green emission
16	CQD ink	Good stability for more than 15 days	Hydrothermal method	228nm.295nm	Strong green emission
17	N/S-CQD ink	No photobleaching	Hydrothermal method	257nm	Strong blue emission
18	CD/NaLuF4	High photostability	Hydrothermal method	365nm	Bright blue emission
19	S/N-GQD	Good photostability for long time	Hydrothermal method	362nm,395nm	Blue and green emission respectively
20	Boron carbon oxynitride dots	Long photostability	Hydrothermal method	320nm	Strong blue colour
21	Si doped CD	Highly photostable	Hydrothermal method	410nm	Orange emission

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Chapter 5

Instruments

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Apparatus

5.1 Photoluminescence Spectroscopy (PL)

5.1.1 Introduction

Photoluminescence (PL) spectroscopy is a simple and direct, non-destructive method. By using this method, you can determine a material's band gap, impurity level, defect detection, recombination mechanism, surface structure, fluorescence property, and its excited states. Photoluminescence spectroscopy is performed in the non-contact mode. It is a non-destructive method of examining a material's electronic structure. In simple terms, it is an instrument that interacts with light and matter.

5.1.2 Basic Principle

When light strikes a sample, the excess energy is absorbed by the material. This is referred to as photo-excitation. One method by which the sample dissipates this excess energy is light emission, also known as luminescence. Photoluminescence is defined as luminescence caused by photo-excitation. When a material is excited, the electrons in the material occupy the allowed excited states. To return to their stable, i.e., equilibrium or ground state, these excited electrons dissipate the excess energy in the form of light (radiative process) or any non-radiative process. The energy difference between the two electronic states involved in the transition between excited and equilibrium states is proportional to the emitted light energy (photoluminescence). The proportion of the radiative process determines the amount of light emitted.

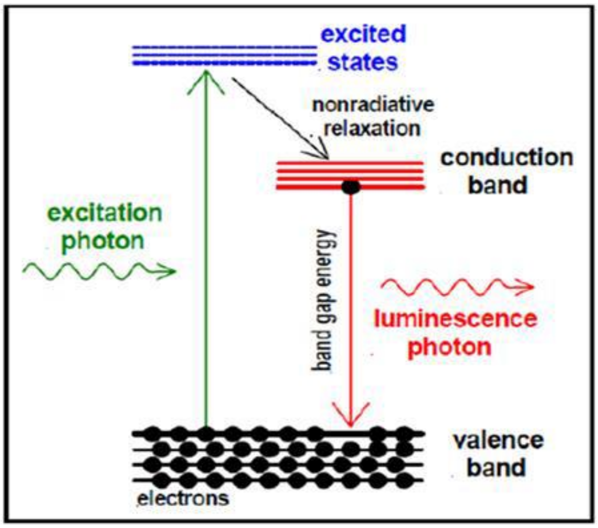

FIGURE 5.1: Basic Principles of PL Spectroscopy

5.1.3 Photoluminescence Different Modes

- **Resonant radiation:** A specific wavelength photon is absorbed in this process, accompanied by the instantaneous emission of an equivalent photon. This process has no discernible internal energy transitions between absorption and emission, and the time scales are on the order of 10 nanoseconds.

- **Fluorescence:** When the chemical substrate initiates the internal energy transition by emitting photons before restoring to its ground state, a certain joule of absorbed energy is liberated, resulting in the emitted light having less energy than the absorbed. One of the known mechanisms with a lifetime of 10-8 to 10-4 s is fluorescence.

- **Phosphorescence:** It is a radiation-based transition in which the absorbed energy undergoes an electronic transition with multiple spin states, i.e., intersystem crossing (ISC). The lifespan of the phosphorescence phenomenon is typically 10-4 - 10-2 s, which is significantly longer than the Fluorescence lifespan. Thus, phosphorescence occurs less frequently than fluorescence because the molecule in its triplet state has a greater chance of experiencing intersystem crossing to a lower energy state prior to the occurrence of phosphorescence.

5.1.4 Spectroscopy

When light is focused on the material, electrons within it can migrate into permitted excited states. When these electrons return to their equilibrium states, the excess energy is released, which may or may not involve the emission of light (a radiative process) (a non-radiative process). The energy of the produced light is determined by the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state (photoluminescence). The amount of light emitted is proportional to the proportionate contribution of the radiative process. In most cases, the released light has a longer wavelength than the absorbed radiation and thus contains less energy.

When the absorbed electromagnetic radiation is sufficiently strong, one electron can absorb two photons, resulting in the emission of light with a shorter wavelength than the absorbed energy. When the released radiation has the same wavelength as the absorbed light, resonance fluorescence occurs. Photoluminescence occurs when radiation is absorbed in the ultraviolet part of the spectrum, which is invisible to the human eye, and the released light is in the visible range. S0 is the ground state of a fluorophore (fluorescent molecule), while S1 is the first (electronically) excited state. S1 is a molecule that can relax in several ways.

It can undergo non-radiative relaxation, in which the excitation energy is transferred to the solvent as heat (vibrations). Excited organic molecules can also relax by converting to a triplet state, which can then relax via phosphorescence or a secondary nonradiative relaxation process.

An S1 state can also relax as a result of interaction with a second molecule via fluorescence quenching. Molecular oxygen (O2) is a highly effective fluorescence quencher due to its unique triplet ground state.

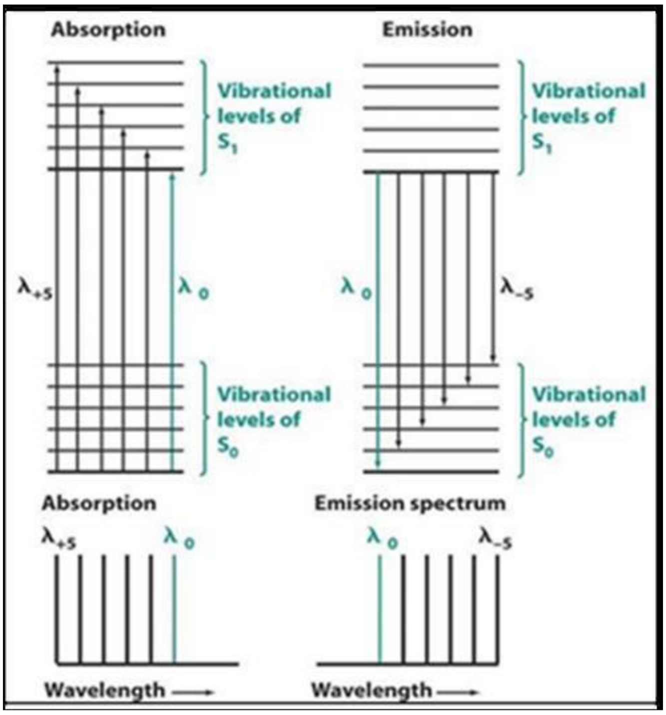

FIGURE 5.2**:** Representing the energy-level diagrams which mention why structure is seen in the absorption as well as emission spectrum and also why the spectra are roughly mirrored images of each other.

5.1.5 Relation between Absorption and Emission Spectrum

Fluorescence and phosphorescence are more likely at lower energies than absorption (the energy of excitation). In the case of absorption, λ0 wavelength denotes the transition from the ground state of vibration, i.e., S0 to S1. When S1 molecules are excited vibrationally, they move to a lower vibrational level before emitting radiation. At λ0 wavelength, a very high cascade of peaks occurs at a higher wavelength. Both the emission and absorption spectra are likely to have a mirror image relationship if the spacing of vibrational levels is roughly equivalent and the probability of transition is similar. λ0 transitions do not completely overlap. In addition to solvation, a radiation-absorbing molecule that is mostly in its ground state, S0; has a solid geometry. Transitions between electronic states are quicker than atoms' vibrational movement or solvent molecules' translational movement; once the radiation is absorbed, the S1 stimulated molecule retains its geometry and solvation S0 state.

Geometry and solvation are both altered to the greatest extent possible soon after stimulation. This rearrangement reduces the excited molecule's energy. When an S1 molecule fluoresces, it returns to its original S0 shape and solvation. This unbalanced configuration must have more energy than an S0 molecule with S0 geometry and solvation. The net result is depicted in the Figure, where the excitation energy exceeds the emission energy.

5.1.6 Instrumentation of Photoluminescence

A spectrofluorometer is an analytical equipment that records and measures the fluorescence of a sample. To record the fluorescence, the excitation, emission, or both wavelengths are scanned. The investigation of signal deviation with regard to time, temperature, concentration, polarisation, or other variables is studied using extra attachments.

The fluorescence spectrometer's block diagram is shown below. Fluorescence spectrometers use monochromators (wavelength selectors), laser sources (sample illumination), detectors, and corrected spectrums.

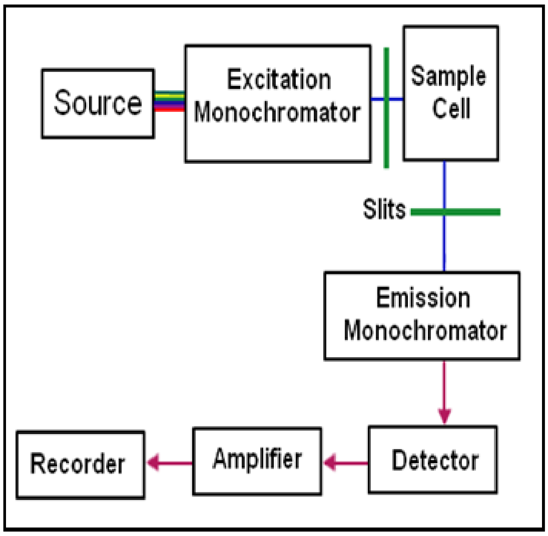

FIGURE 5.3: Instrumentation of Photoluminescence

- **Source of Illumination:**

A continuous type, 150 W ozone-free xenon arc lamp is used as the light source. The light from the lamps is collected by a diamond-turned elliptical-shaped mirror, which is then directed into the entry slit of the excitation monochromators.

A quartz-based window is utilised to segregate the excitation monochromator from the lamp's housing, which vents heat out of the device and protects against the lamp's rare failure. The ability to resolve the entire spectrum stretches and decreases spherical aberrations and re-diffraction.

- **Monochromators:**

Monochromators are classified into two types: excitation monochromators and emission monochromators. It employs whole reflective optics to maintain high resolution across the entire spectrum while also reducing aberrations (spherical) and re-diffraction.

- **Gratings:**

Reflection Grating is an essential component of a monochromator, whose aim is to scatter striking (incident) light through vertically positioned grooves. Spectra are obtained by rotating gratings with 1200 grooves per mm and being blazed at 330 nm (excitation) at 500 nm (emission). The grating is coated with a protective coating of MgF2 to prevent oxidation.

- **Slits:**

At the monochromator's entrance and exit sites, very flexible slits are used. The incident light's bandpass is defined by the width of the slit on the excitation monochromator, whilst the fluorescence intensity signal is controlled (recorded by the signal detector) by the slits on the emission monochromator.

When determining slit width, the trade-off is signal strength versus spectral resolution. When the slit width is greater, the resolution decreases because more light falls on the sample as well as the detector, but when narrower slits are employed, the resolution increases but at the expense of the signal.

- **Shutters:**

An excitation shutter is installed beneath the exit slit of the excitation monochromator to protect the sample from photobleaching or photodegradation caused by prolonged exposure to light.

The detector is shielded from the bright light by an emission shutter located just before the entry of the emission monochromator.

• Sample compartment:

Several alternative attachments and fibre optic bundles are included in the sample compartment to transport the excitation beam to the remote sample and return the emission beam to the emission monochromator.

• Detectors:

There are two sorts of detectors: signal detectors and reference detectors. The photon counting signal detector is an R928P photomultiplier tube that directs the signal to a photon counting module. The objective of the reference detector is to monitor the xenon lamp for wavelength and time-dependent output adjustment. This detector is based on UV, which increases the silicon photodiode, which is situated just before the sample compartment.

FIGURE 5.4: Horiba Jobin Yvon Fluromax spectrofluorometer

5.1.7 Photoluminescence Spectroscopy Limitations

Even though it is not a qualitative technique, it can be used to identify tiny concentrations of optical centres. The main scientific PL constraint is that some optical centres may have many excited states that are not occupied at low temperatures. Another significant drawback of PL is the disappearance of the luminous signal.

5.1.8 Applications

- **Determination of Band gap:**

In semiconductors with radiative transitions, the band gap denotes the energy difference between the conduction band (top) and the valence band (bottom). The range of a semiconductor's PL spectrum is utilised for non-destructive bandgap analysis. This mode allows you to quantify the composition of the elements in a semiconductor compound as well as material specifications that influence device efficacy, such as solar cells.

- **Identification of level of Impurity as well as a defect:**

When the radiative transition happens in semiconductors, some localised defect levels are induced. The photoluminescence energy can identify specific flaws associated with these levels, whereas the PL quantity can determine their concentration. The photoluminescence spectra of the sample at low temperatures frequently display spectrum peaks associated with impurities existing inside the host material. Highly sensitive Fourier transform photoluminescence micro spectroscopy has the potential to detect very minute amounts of planned and unexpected impurities, which have a significant impact on material quality and device performance.

• Recombination phenomena:

Both radiation and non-radiation processes involve the "recombination" mechanism (Return to equilibrium). The amount of PL material emitted is directly related to the relative amount of radiative and nonradiative recombination rates.

The amount of PL and impurities is typically associated with nonradiative rates, and it is reliant on the photo-excitation intensity as well as temperature, both of which are directly related to the dominant recombination mechanism. As a result, qualitative PL analysis includes tracking changes in material quality as a function of variables such as growth and processing, which aids in understanding the fundamental physics of the recombination mechanism.

• Surface structure and excited states:

Some widely used conventional methods, such as XRD, IR, and Raman spectroscopy, are frequently insensitive to oxide-supported catalysts with low metal oxide concentrations. Because PL is overly sensitive to surface effects or semiconductor-based particle adsorbed species, it is used as a probe of electron-hole surface processes.

5.2 Diffuse Reflectance Spectroscopy (DRS)

5.2.1. UV-Vis Near-Infrared Spectroscopy:

UV-Visible near-infrared (UV-Vis-NIR) In the ultraviolet-visible spectral region, a spectrophotometer measures optical transmittance, absorbance, and reflectance. Optical transmittance, absorbance, and reflectance in the ultraviolet-visible spectral range are measured using a UV-Vis near Infrared (UV-Vis-NIR) Spectrophotometer.

The percentage of the radiation absorbed, transmitted, or reflected at each wavelength is measured using UV-VIS absorption spectroscopy. Typically, this is achieved by scanning the wavelength range and measuring absorption. It is commonly used in organic chemistry to study the extent of multiple bonds or aromatic conjugation inside molecules. The technique can be extended to gases and solids, as well as beyond absorption to detect reflected light rather than transmitted light.

Light absorption can be described by two fundamental laws:

Lambert's Law - The proportion of incident light absorbed by a transparent medium is independent of the intensity of the light (provided that there is no other physical or chemical change to the medium). Therefore, successive layers of equal thickness will transmit an equal proportion of the incident energy.

Lambert's law can be expressed by: **II0=T**

Where I is defined as the intensity of the transmitted light, I0 is the intensity of the incident light, and T is the Transmittance.

Beer's Law - The absorption of light is directly proportional to both the concentration of the absorbing medium and the thickness of the medium in the light path.

A combination of the two laws (known jointly as the Beer-Lambert Law) defines the relationship between absorbance and transmittance. $\mathbf{A=logI0I=log100T=\varepsilon cb}$

Where, is absorbance (no unit of measurement), molar absorptivity (dm3mol-1cm-1), molar concentration (mol dm-3), and path length (cm).

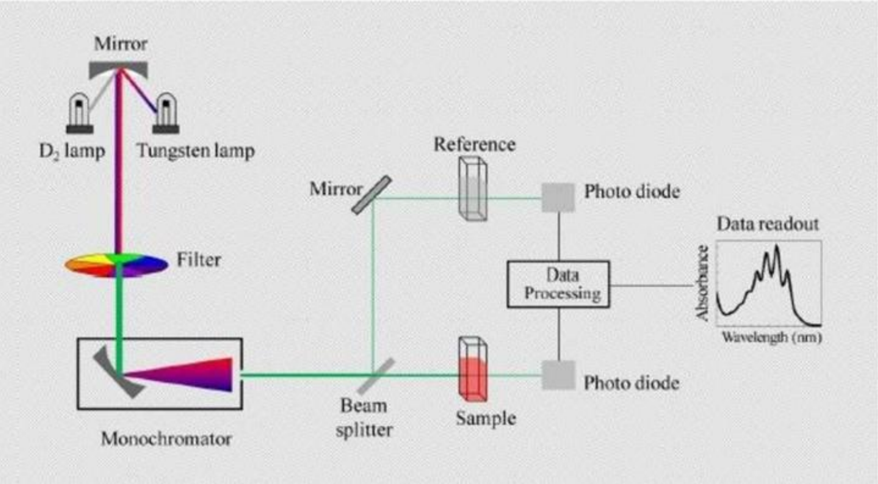

FIGURE 5.5: Basic Principles of UV-VIS Spectroscopy

5.2.2 Light Reflection and Reflectance Spectra:

The spectrometer beam is directed into the sample and reflected, dispersed, and transmitted, resulting in diffuse reflectance (shown on the right). The accessory catches and directs back reflected, diffusely scattered light to the detector optics (part of which is absorbed by the sample). Diffuse reflection refers to the portion of a beam that is scattered within a sample and returns to-

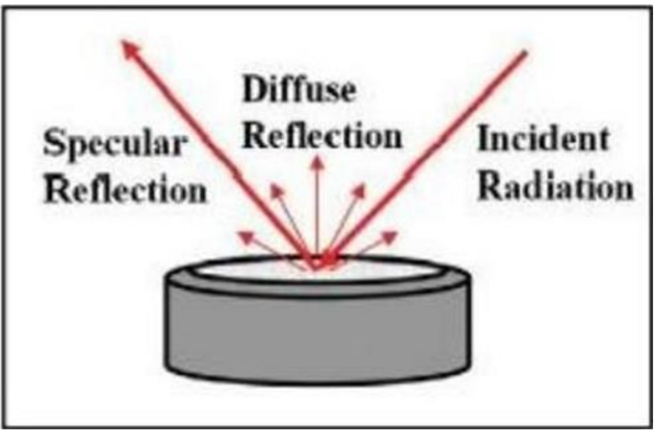

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FIGURE 5.6: Diffusion Reflectance

Other characteristics that contribute to great spectral quality in diffuse reflectance sampling include particle size, refractive index, homogeneity, and packing. Despite all of these sample preparation processes; the raw diffuse reflectance spectra will appear different from their transmission counterpart (stronger than expected absorption from weak IR bands).

To correct these discrepancies, a Kubelka-Munk conversion can be performed to a diffuse reflectance spectrum.

Kubelka-Munk Function: $F=(1-R)2R=kS$

R stands for the sampled layer's absolute reflectance, k for the molar absorption coefficient, and s for the scattering coefficient.

The spectrum above depicts the spectral conversion of ibuprofen acquired using diffuse reflectance.

The Kubelka-Munk transformed spectrum for ibuprofen compares well to the transmission spectrum and is readily detected using a transmission spectral database library search.

Diffuse reflectance spectroscopy (DRS) of (nanoscaled) powders is a frequently used and powerful instrument in material sciences and industry. An input light beam's scattered intensity is scanned over the sample as a function of wavelength, and the resulting data set is analysed in terms of macroscopic optical properties such as total reflectivity.

Furthermore, DRS has the capacity to detect particle absorption characteristics even at sub-micron length scales. Absolute values of the absorption coefficient, as well as dispersive qualities, are crucial for a variety of materials with strong commercial potentials, such as pigments or phosphors. Absorption qualities influence the macroscopic optical properties of dielectric powders, but they also influence the losses of internally emitted light.

As a result, DRS is routinely utilised in applications that fall short of its capabilities, and it is mostly used to determine macroscopic optical properties. The purpose of this study is to provide end-to-end guidance from sample preparation to absorption spectra determination by tackling the tough challenge of optical characterization of pure, dielectric (nano-)powders.

The introduction of a new powder pellet preparation technique that enables for the manufacture of samples with excellent Lambertian scattering behaviour that are also highly reproducible is highlighted. As a result, thick, non-translucent samples are used to enable dependable experimental access to diffuse reflectance spectroscopy and subsequent absorption coefficient determination.

This method offers various advantages, including

1) high-quality reflectance spectra,

2) good consistency in calculating absorption features, and

3) easy identification of signal artefacts, allowing for further reduction.

5.2.3 Measurement Setup:

5.2.3. (a) Requirements and Procedures

A specialised optical setup is necessary for reliable and reproducible measurements of diffuse reflectance spectra. While it is possible to create it from scratch and acquire satisfactory results, numerous dedicated spectrometers for greater precision measurements are commercially available at the time of writing this research. Naturally, successor or previous models are also appropriate, depending on their characteristics and measurement choices.

5.2.3. (b) Components of Diffuse Reflectance Spectrophotometer

A spectrophotometer consists of the following components

- A source of radiation of appropriate wavelengths
- Monochromator and optical geometry
- Filter Sample compartment
- Detector, Photomultiplier, Measuring system, Computer

Because double-beam spectrometers simultaneously detect the sample and the white standard, calculating the diffuse reflectance of non-luminescent substances is straightforward, fast, and precise. Because of the parallel acquisition process, lamp intensity changes are not a concern. Extraneous light emission at wavelengths other than the excitation wavelength generates erroneous extra signals in fluorescence, rendering an unfiltered diffuse reflectance spectrum incorrect. Using a fluorescence spectrometer, on the other hand, gives you the distinct advantage of being able to readily do diffuse reflectance measurements on any material.

Such a scenario is now omitted in favour of a collimated (or, optionally, defocused) beam. For fluorescent samples, a configuration with two independent monochromators is required: The excitation monochromator selects a wavelength for sample illumination, while the emission monochromator transmits the linear diffuse reflectance of the sample, cancelling any further fluorescence emission.

FIGURE 5.7: UV-VIS-NIS (SHIMADZU UV-3600) Spectrophotometer

As a result, this mode of operation, in which both monochromators are set to the same wavelength, is generally referred to as synchronous scanning. In addition to monochromators, additional spectral filters remove potential higher diffraction orders transmitted by grating-based monochromators, as well as sample fluorescence. If only monochromatic illumination is required, the light source/monochromator combination can be replaced by a suitable laser or bandpass filtering behind a broadband emission source.

If intensity fluctuations are a significant problem, such as due to lamp power drifts or ambient temperature changes, it is advisable to separate a small amount of the excitation light into a low-drift reference detector. The remainder of the material will be used to illuminate the samples. The reference detector's signal can then be utilised to scale the measured diffuse reflectance intensities. Any extra detector, however, will eventually increase overall electronic noise and should so be utilised with prudence.

When compared to vertically placed samples, which are common in integrating spheres where an additional cover window is frequently used to keep the powder in place, horizontal alignment of the powder sample has the distinct advantage of eliminating potential spectrometer contamination due to material gliding off of the (brittle) surface.

Even without a cover window, the horizontal alignment ensures that the sample is preserved throughout the measurement and that contamination of its surroundings is avoided. A parallel excitation/emission beam geometry also eliminates specular reflection losses caused by a slight tilt of the incident light direction relative to the sample surface normal. This significantly reduces the impact of sample surfaces that aren't perfectly Lambertian. The beam path requires at least one additional mirror to reflect the excitation beam downwards onto the sample to account for this geometry. This mirror also relays the emission beam towards the detection arm in an optimised setup.

The sample's diffusely reflected light is directed into the optical detection path and then recorded by a detector within the spectrometer, such as a photomultiplier tube (PMT). We'll stick to single-channel detection for the sake of simplicity.

5.2.4 White Standards

Experimenting with precise, absolute values for diffuse reflectance of a sample is difficult in general. It invariably necessitates a thorough understanding of the used spectrometer, particularly its optical transfer function. The use of reference materials with well-documented diffuse reflectance is a common method for investigating the peculiarities of spectrometers and for calibration purposes. The diffuse reflectance of such white standards is characteristic over a wide spectral range.

From both the diffuse intensity signal of sample Is and the white standard Iws, the diffuse reflectance R = Is/Iws is calculated. Historically, white standard materials have been micro- and nano-scaled powders of magnesium oxide (MgO) and barium sulphate ($BaSO4$), which have a pronounced and spectrally homogeneous diffuse reflectance in the visible spectrum. Following that, a typical three-fold scan would consist of:

1. Determine the white standard.
2. Take a sample and measure it.
3. Determine the white standard.

5.3 Morphological Analysis:

5.3.1 FESEM

The scanning electron microscope (SEM) is one of the most flexible tools for examining and analysing the morphology of microstructures. SEM utilises a focused electron beam to scan across the surface of the specimen systematically, producing large numbers of signals. These electron impulses are transformed into a visual signal that is shown on a cathode ray tube (CRT). The electron beam can be generated by two ways:

a) Thermionic emission; b) Field emission.

The thermionic emission is by controlling the electron emission from the source using thermal energy. Field emission electron guns (FEG) are an excellent alternative to thermionic electron guns in contemporary electron microscopes.A FESEM is used to visualized very small topographic details on the surface or entire or fractioned objects. This method is used by biologists, chemists, and physicists to study structures as tiny as 1 nanometre (= billionth of a millimetre). The FESEM may be used to investigate organelles and DNA material in cells, as well as synthetic polymers and microchip coatings.

Sample Preparation:

Since the SEM is operated under high vacuum the specimens that can be studied must be compatible with high vacuum (~ 10-5 mbar). This implies that liquids and materials containing water or other volatile components cannot be directly examined. Fine powder samples must also be securely attached to a specimen holder substrate in order to avoid contamination of the SEM specimen chamber.Non-conductive materials must be connected to a conductive specimen container and sprayed or evaporated with a thin conductive layer.Au, Pt, Pd, and their alloys, as well as carbon, are common coating materials.

Components of FESEM:

Electron Guns:

Modern SEM systems demand a steady electron beam with high current, small spot size, tunable energy, and low energy dispersion from the electron gun. In a SEM system, several types of electron guns are utilised, and the quality of the electron beam generated by each differs significantly. The original SEM systems employed tungsten "hairpin" or lanthanum hexaboride (LaB6) cathodes, but field emission sources which give more current and reduced energy dispersion, are now the norm. Another essential factor to consider while choosing electron sources is the lifespan of the emitter.

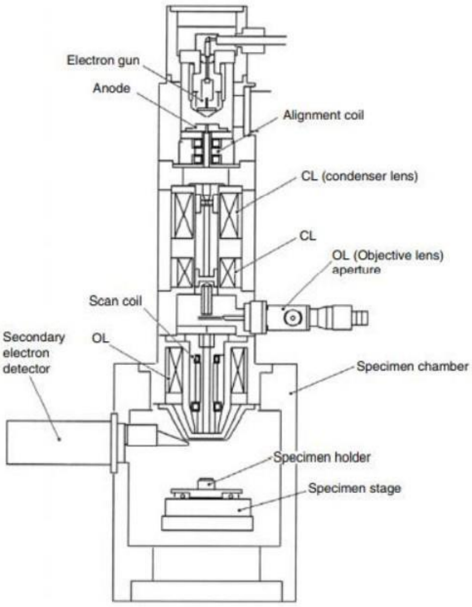

FIGURE 5.8: Schematic Diagram of FESEM

Electron Lenses:

Electrostatic or magnetic fields can concentrate electron beams.However, because an electron beam controlled by a magnetic field has less aberration, the SEM system only uses a magnetic field. The electrons' paths may be changed using electromagnets.

Condenser lens:

After passing through anode plate from the emission source, the electron beam will diverge. The condenser lens converges and collimates the electron beam into a nearly parallel stream. A magnetic lens is made up of two rotationally symmetric iron pole pieces with a magnetic field provided by a copper winding. Pole pieces have a hole in the middle that allows the electron beam to pass through. The magnetic field influences (focuses) the electron beam through a lens-gap that separates the two pole components. The focus point location may be adjusted by changing the condenser lens current.

Scan Coils:

The electron beam is deflected in a zigzag pattern by the scan coils as it passes over the item. This scan movement is synchronised with the creation of the image on the display. The refresh rate on the screen and the level of noise in the image are determined by the scan velocity. Upper and lower coils are commonly used in scan coils to prevent the development of a circular shadow at low magnification.

The Objective Lens:

Below the condenser aperture, the electron beam will diverge. Using objective lenses, the electron beam is focused into a probe point on the specimen surface, as well as giving further demagnification. As Fundamentals of Scanning Electron Microscopy 15 and aperture size, the diameter of the electron beam on the specimen surface (spot size) is reduced, which improves picture resolution.

The Stigmator Coil:

The stigmator coils are used to rectify inconsistencies in the beam's x and y deflection, resulting in a perfectly round beam.

When the beam is ellipsoidal rather than circular, the picture seems fuzzy and stretched.

Object Chamber:

The item is then placed on a specific holder after being coated with a conductive coating. The item is introduced into the high vacuum portion of the microscope through an exchange chamber and anchored on a movable stage. In the chamber, the secondary electron emission detector (scintillator) positioned at the back of the object holder.

Figure 5.9: FESEM (Hitachi S-4800) set up

Image Formation

When an electron beam in a SEM impinges on a specimen surface and excites different signals for SEM inspection, complex interactions occur. Secondary electrons, back scattered electrons (BSEs), transmitted electrons, and specimen current may all be gathered and shown on monitor. The excited x-ray or Auger electrons are examined to get information about the specimen's composition. In this section, we'll go over the electron beam's interactions with the specimen surface as well as the principle of picture creation using various signals.

5.3.2 X Ray Photoelectron Spectroscopy (XPS)

X-Ray Photoelectron Spectroscopy is one of the most powerful surface analytical techniques capable to provide accurate qualitative elemental analysis (for all elements except hydrogen and helium), quantitative composition and determination of chemical states such as binding and oxidation can also be done. The information should be originated within ~10 nm from the outer surface.

5.3.2.1 Principle of XPS

XPS is based on the photoelectric effect which is discovered by Hertz in 1887. In this case, electron emission from the surface is resulted due to the interaction of an x-ray photon of sufficient energy with the solid surface. The applied x-ray of 1-15 KeV energy is capable to induce electrons not only from the outer shells but also from the core levels of all elements of periodic table. The governing equation of this phenomenon is as follows:

$$h\nu = Eb + Ekin + Wf$$

Where Eb is binding energy, Ekin is the kinetic energy of the photoelectron, Wf is the work function of the instrument.

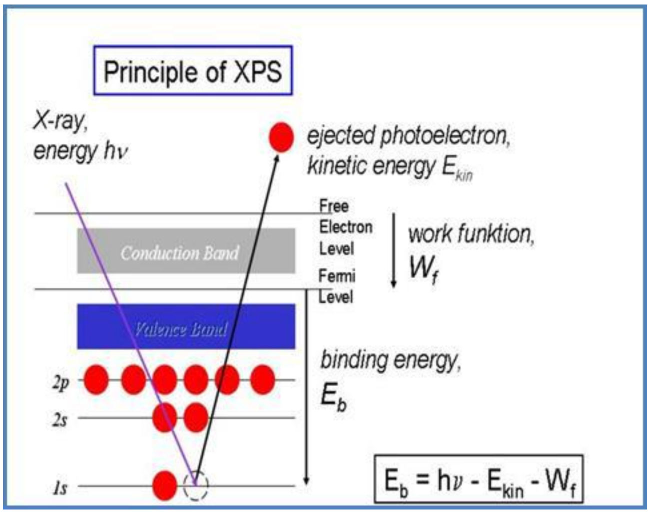

FIGURE 5.10: XPS Principle

5.3.2.2 Configuration of XPS instrument

The experimental set-up contains mainly the following parts: (i) an X-ray source for XPS, (ii) an electron energy analyzer, combined with a detection system, and (iii) a sample stage, all contained within a vacuum chamber. As for most techniques, the system is operated and controlled by a computer, usually provided a software allowing mathematical treatment.

- **X-ray source**

Since XPS is concerned with the analysis of core electrons from a solid surface, sources used in XPS must be able to produce photons of sufficient energy to access a suitable number of core electron levels. Photons of this energy lie within the X-ray region of the electromagnetic spectrum. As a result, these are otherwise referred to as X-rays. X-ray tubes produce X-rays by directing a sufficiently energetic electron beam at some metallic solid. This metallic object is referred to as the X-ray anode, with the electron source being the cathode. Although any solid can in principle is used as an X-ray anode, Al has become the most used in XPS due to the relatively high energy and intensity of Al-Kα X-rays, the minimal energy spread of Al-Kα X-rays and the fact that Al is an effective heat conductor.

• Electron energy analyzer

Since the information in XPS is derived from the Ekin of the electron emissions, effective analysis requires an energy filter that exhibits both a high-energy resolution and a high transmission. The former allows for the separation of closely spaced peaks, thereby optimizing speciation identification capabilities, while the latter allows for sensitivity to be maximized. The two primary energy filter configurations used in XPS named Cylindrical Mirror Analyzer (CMA), and Concentric Hemispherical Analyzer (CHA).

• Detector

In XPS, it is not only important to measure the energy of the electron emissions but also the number of electrons produced. XPS spectra are plotted in units of energy versus intensity, with the energy defined by the energy analyzer used and the intensity defined by the number of electrons recorded by the detector. To obtain the best possible sensitivity, the detector must be capable of recording individual electrons, that is, operating in pulse counting mode. This signal is recorded in units of current (A), which are then represented in units of counts per second.

Sample stage

The mounting of the samples on the sample holder should be done in such a way that electrical conduction is guaranteed. This is achieved by using metallic clips or bolt-down assemblies. Alternatively, metal-loaded tape may also be used. In the case of powders, the particles can be pressed into an indium foil or carbon tape.

Vacuum requirement

As XPS is a surface-sensitive method, impurities can play a major role in the observed spectra. The criterion is that a good vacuum is needed to maintain the integrity of the surface. In general, 10-5Torr is sufficient to allow the Photoelectron to reach the detector without suffering collisions with other gas molecules. On the other hand, 10-9Torr or lower is required to keep an active surface clean for more than several minutes. So, 10-8 - 10-9Torr provides a reasonable pressure range for XPS measurement. Sample analysis was performed on the SPECS with a hemispherical energy analyzer (HAS 3500). Photoelectrons were excited using the monochromatic Mg Kα X-ray (1253.6eV) or Al Kα X-ray (1486.6eV) was used as the excitation source operated at 10 kV and with an anode current 17 mA.

Chapter 6

Experimental Process

&

Result Analysis

6.1 Synthesis of Carbon Dots

Briefly, 2 g piperazine and 1 g phthalic acid were weighed in the 100 mL beaker, then 5 mL deionized water was added. After a few minutes of ultrasound, a turbid mixture was formed. Then the beaker was placed at the centre of the rotation plate of a domestic microwave oven (700 W) and heated for 3 min. After cooling down, the solid CDs were obtained. Without further purification steps, the powdery CDs (named as p-CDs) can be directly obtained by gently grinding the solid CDs in quartz mortar.

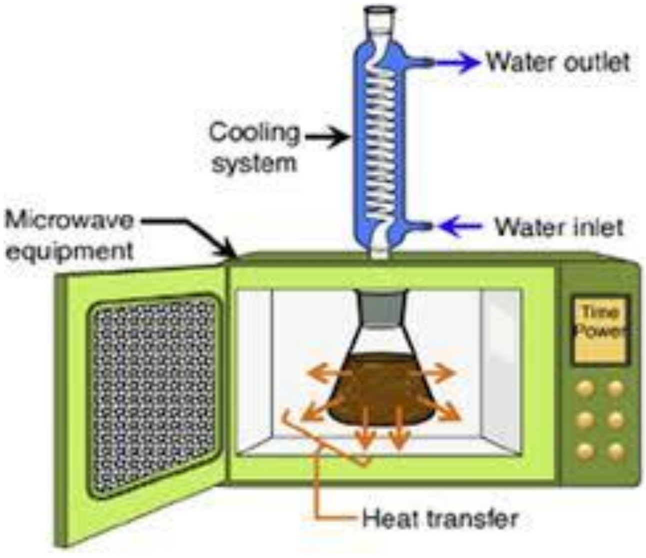

FIGURE 6.1: Microwave Synthesis Setup

6.2 Ink Development

0.7g of Polyvinyl Alcohol (PVA) was added into 10ml of DI water to act as a binder for the ink. In subsequent stages PVA was replaced by Polyacrylic Acid (PAA) & Polymethyl Methacrylate (PMMA). Later, 0.3g Sodium dodecyl Sulphate was added as a surfactant to improve the ink performance. In the final step, 3ml of the liquid carbon dot (fluorescent material) was added to obtain the desired ink. The whole system was stirred at 500 rpm for 3 hours.

6.3 Optical Analysis

Photoluminescence and UV-vis spectra were used to evaluate the optical characteristics. CDs exhibit unusual absorption and luminescence characteristics due to their simple capture nature and look. CDs are usually expressed as a significant absorption peak in the deep UV region caused by the p-p* transition. At a higher wavelength, the tiny absorption peaks associated with the n-p* transition may also be seen. The CD core and indefinite chemical groups are held together on the surface of CDs, and so the photoluminescence is organized by the CD core and neighbouring chemical groups. CDs' basic qualities are mostly determined by their form, size, and edge structure, and they play an active role in the location of absorption peaks.

6.3.1 UV Visible Spectroscopy

Ultraviolet-visible spectroscopy is reflectance spectroscopy and absorption spectroscopy comprising of the ultraviolet and the adjacent full visible regions of electromagnetic spectrum, i.e., it uses light in the visible and the adjacent ranges. The reflectance or absorption in the visible range directly affects the perceived colors of the chemicals involved. In this region of the spectrum atoms and molecules undergo electronic transitions. Absorption spectroscopy is complementary to fluorescence spectroscopy. Fluorescence deals with the transition from the excited state to the ground state whereas, absorption deals with the transition from ground state to the excited state. UV-Vis spectroscopy is widely used in analytical chemistry for determining the constituting analytes, like transition metal ions, highly conjugated organic compounds, and biological macromolecules. Spectroscopic analysis is usually done in solutions but solids and gases may also be studied using this. It can also be used to determine kinetics or the rate of a chemical reaction. UV-VIS spectroscopy provides the extent of absorption and reflectance in a sample.

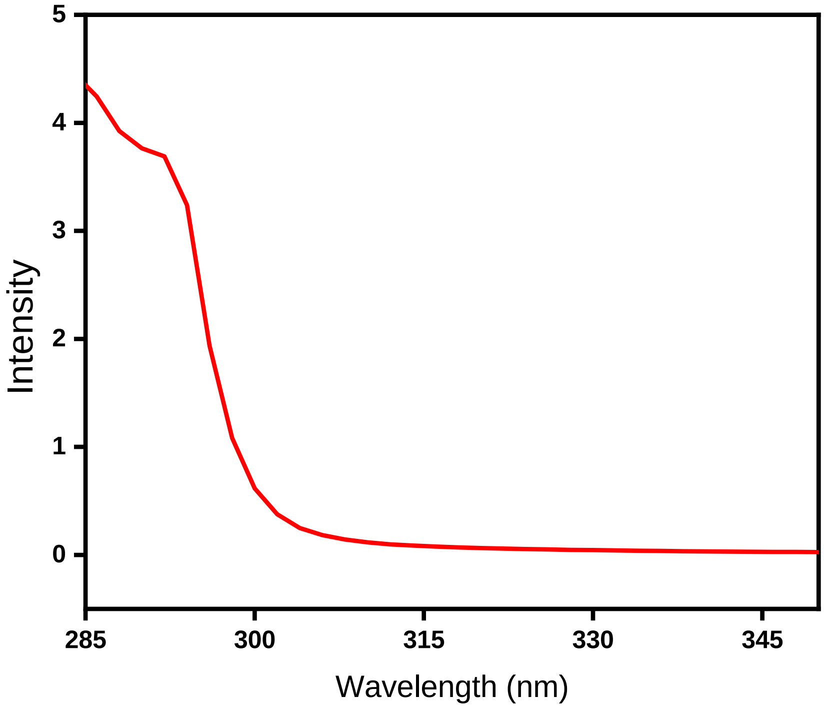

FIGURE 6.2: UV-Vis Spectroscopy of Carbon Dots

6.3.2 Photoluminescence Spectroscopy

Photoluminescence (PL) happens when light energy or photons excite any substance, resulting in photon emission. The process is summarised as follows: light is focused onto a sample, where it is absorbed, and photo-excitation occurs. As a result of photo-excitation, the electron jumps to a higher energy state and subsequently relaxes to a lower energy state, releasing energy as photons. The light emitted as a result of this process is known as photoluminescence (PL). PL can be used to measure band gap, impurity levels and defect detection, recombination mechanism, material quality, and molecular structure and crystallinity.

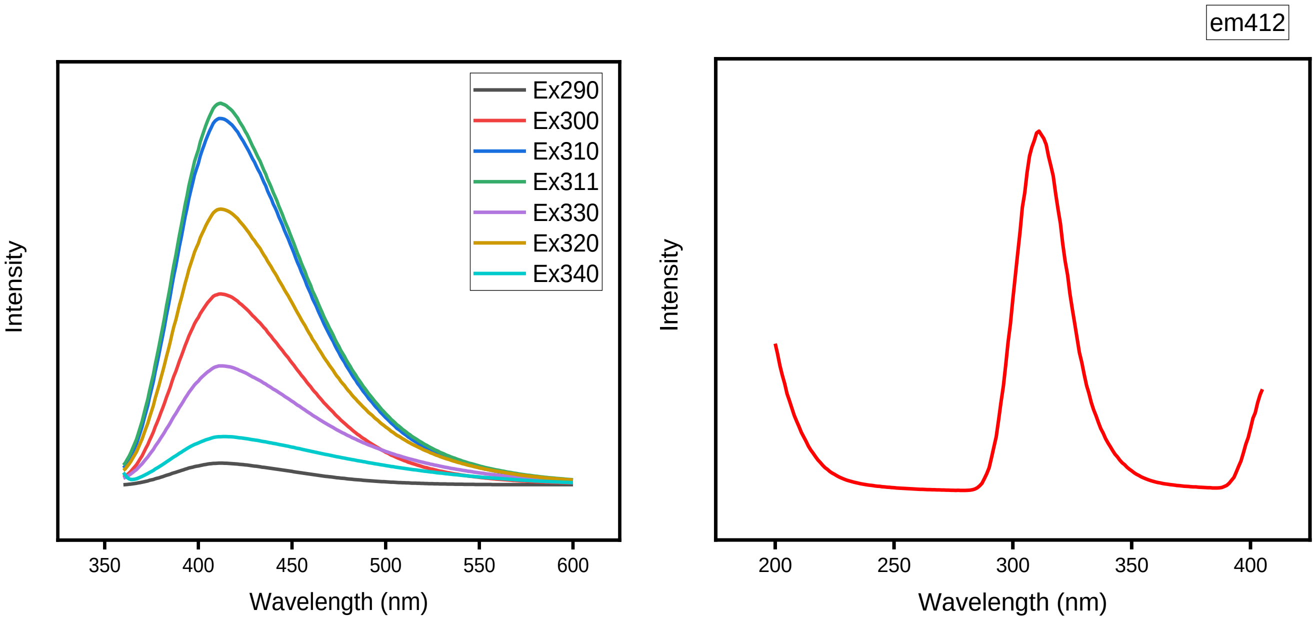

FIGURE 6.3 (A) & (B): Photoluminescence Spectroscopy of Carbon Dots

In photoluminescence spectroscopy, we provide excitation energy through various wavelengths. From the plot A we can see that the highest peak is obtained for excitation wavelength of 311nm. The resultant wavelength is obtained at 412nm.

In plot B, the emission spectrum is tallied with the excitation spectrum of the sample when the same amount of emission spectrum is provided to receive the former excitation energy. In order to verify the above emission spectrum, an emission spectrum of 412nm is provided in response to which an excitation wavelength of 311nm is received, which is same as that of the previous result of the sample This process verifies the stability of the band gap.

6.3.3 Bandgap Analysis

From tauc plot, we can calculate the bandgap of the carbon dots.

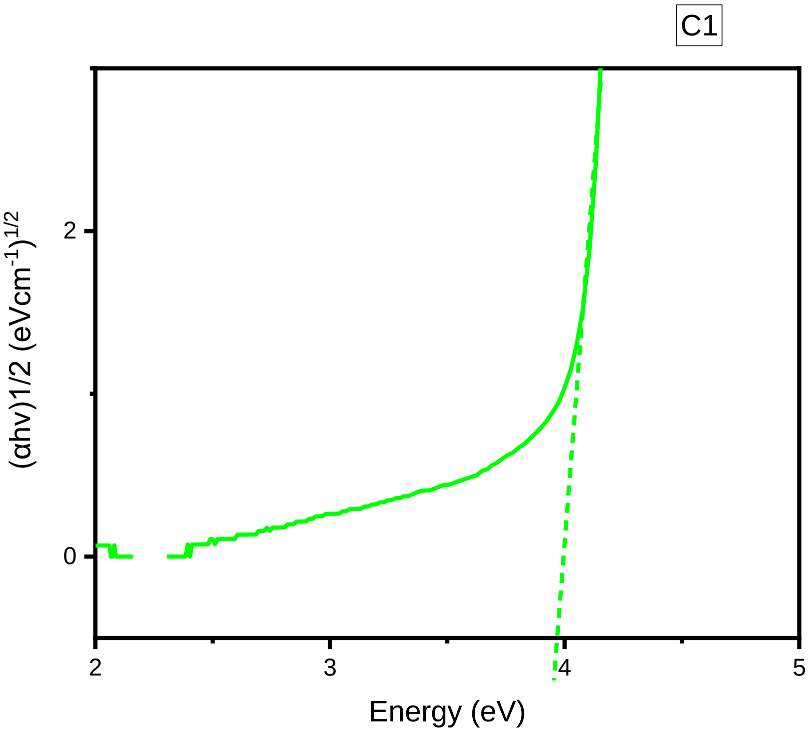

FIGURE 6.4: Tauc plot of Carbon Dots

Hence, the obtained bandgap is 3.98eV.

We can cross check the obtained bandgap from Tauc plot with following method

Egopt = 1240 nm/λonset was used to compute the optical bandgap from the onset wavelength of absorption, where Egopt is the optical bandgap and λonset is the onset wavelength of absorption.

λonset = 311nm from the Photoluminescence spectroscopy plot A.

Egopt = 1240/311=3.98 eV.

The bandgap of CDs at 311 nm wavelength is 3.98 eV.

6.4 Morphological Analysis

X Ray Diffraction, Field Emission Scanning Electron Microscopy (FESEM), High-resolution transmission electron microscopy (HRTEM), Fourier Transform Infrared Radiation (FT-IR) and X-ray photoelectron spectroscopy (XPS) were used for structural and compositional studies.

6.4.1 X Ray Diffraction (XRD)

X-ray diffraction analysis (XRD) is a technique used in materials science to determine the crystallographic structure of a material. XRD works by irradiating a material with incident X-rays and then measuring the intensities and scattering angles of the X-rays that leave the material [1]. A primary use of XRD analysis is the identification of materials based on their diffraction pattern. As well as phase identification, XRD also yields information on how the actual structure deviates from the ideal one, owing to internal stresses and defects

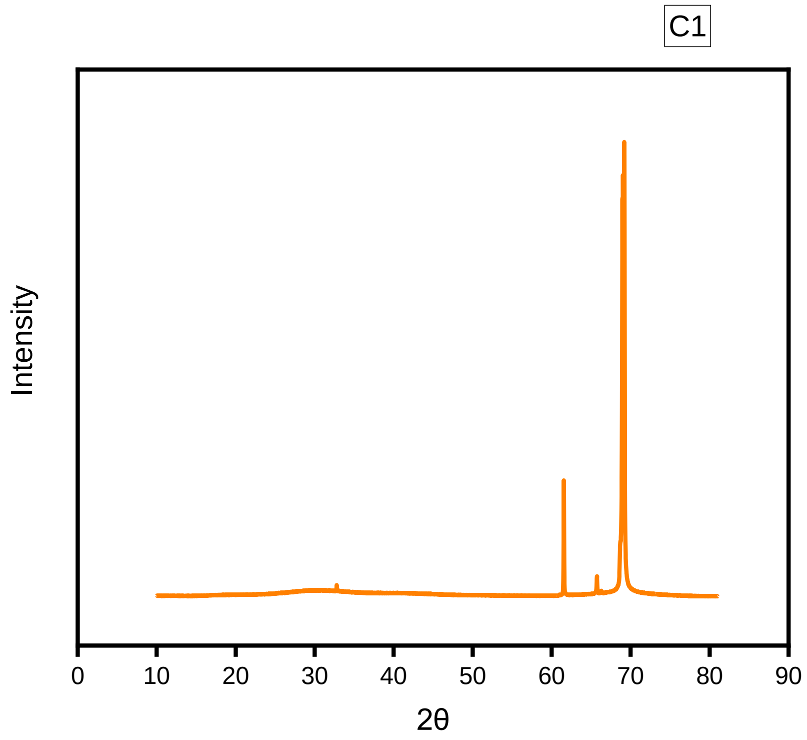

FIGURE 6.5: XRD Pattern of Carbon Dots

From the XRD pattern, two sharp diffraction peaks are obtained at 2θ= 61°, 70° due to the presence of Si wafer substrate on which the sample was deposited.

At 2θ= 32° and 65°, a diffraction peak is obtained which indicates that the carbon quantum dots are composed of small crystalline core with disordered surface [1].

6.4.2 XPS Analysis

X-ray photoelectron spectroscopy (XPS) analysis shows the composition of as-synthesized Carbon Dots. Carbon and Nitrogen was found in the sample from the XPS spectrum as shown in Figure.

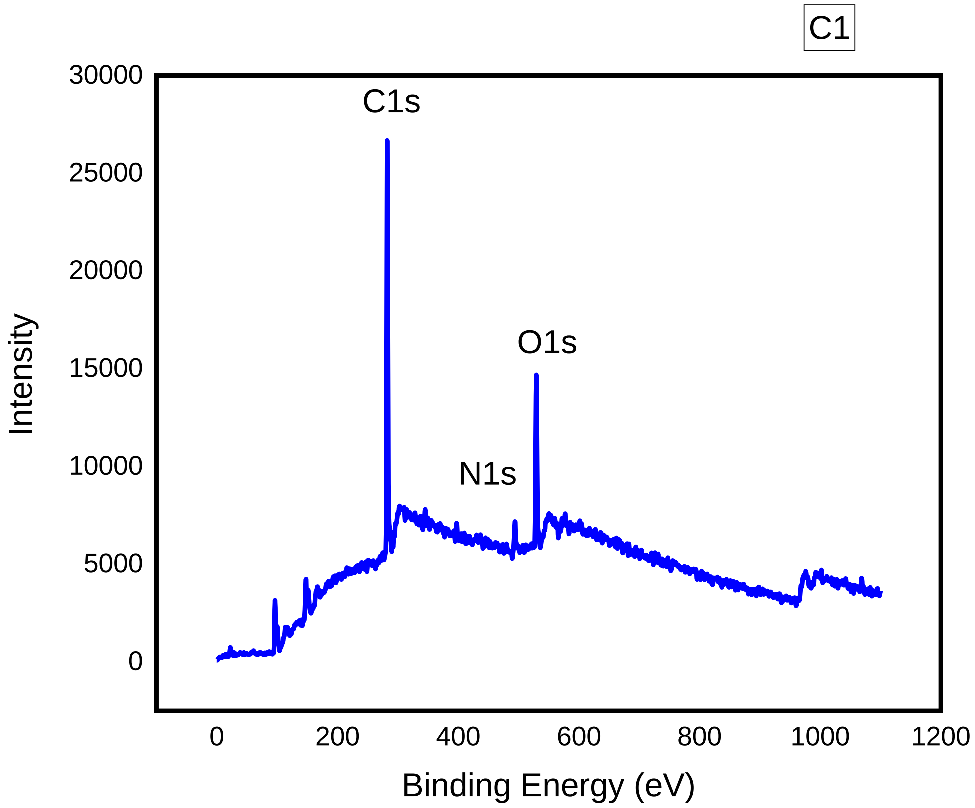

FIGURE 6.6: XPS Analysis of Carbon Dots

The full-scan XPS spectrum of the CDs shows three prominent peaks corresponding to C1s ~284.5 eV, N1s ~497.3 eV and O1s ~530.3 eV. In the high-resolution spectra, the C1s band can be mainly resolved into three peaks at 284.7 eV, 285.9 eV and 287.8 eV, correspond to C–C/C=C and C–O/C-N respectively.

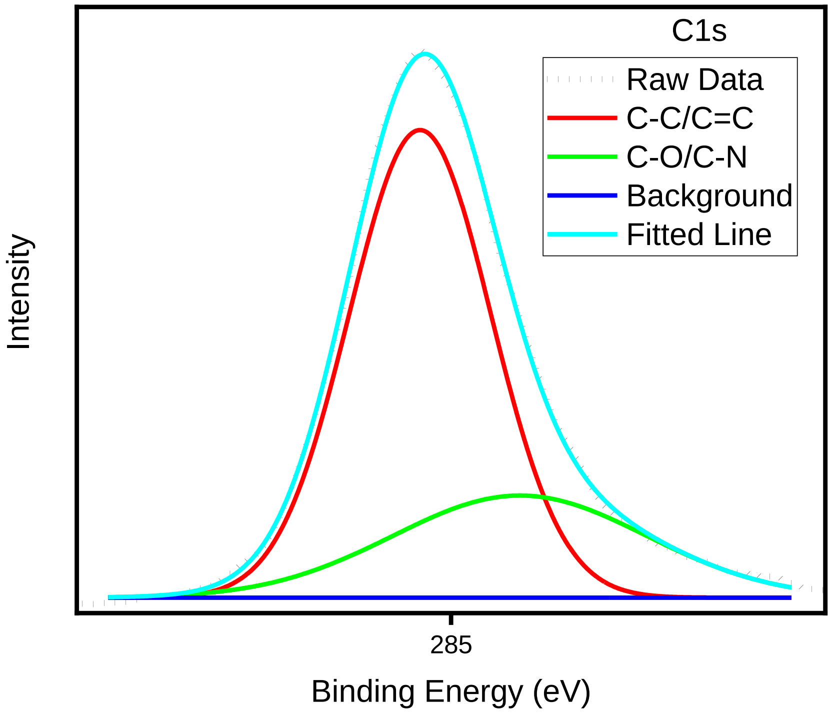

FIGURE 6.7: High Resolution Spectra of C1s

6.4.3 HRTEM

The length and orientation of the CDs layers can be easily expressed using HRTEM image processing technologies. HRTEM is a legitimate diffraction device that may be used to directly observe the morphological properties of a substance while also getting a great amount of microcrystalline structure information [4].

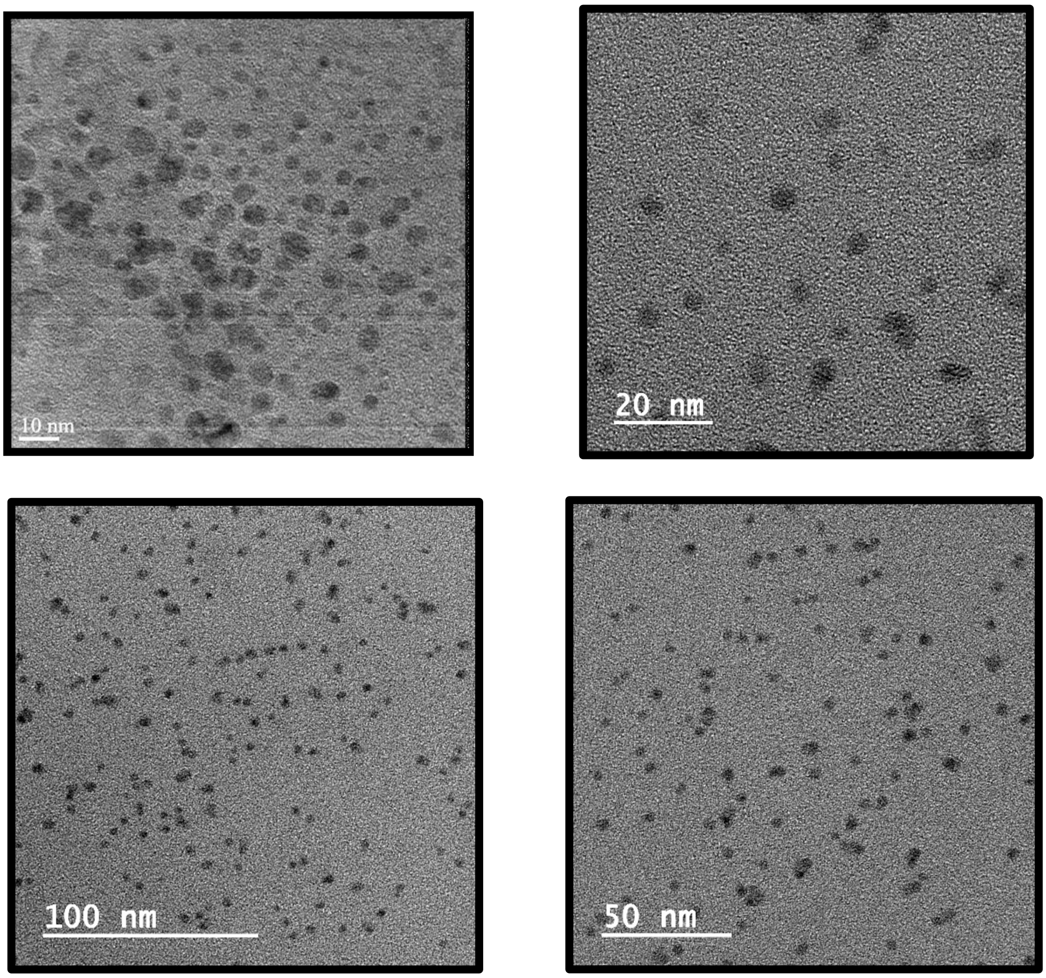

FIGURE 6.8: HRTEM images of Carbon Dots

6.4.4 FTIR Spectroscopy Analysis

FTIR spectroscopy is an established technique for quality control when evaluating industrially manufactured material, and can often serve as the first step in the material analysis process. A change in the characteristic pattern of absorption bands clearly indicates a change in the composition of the material or the presence of contamination. If problems with the product are identified by visual inspection, the origin is typically determined by FTIR microanalysis. This technique is useful for analyzing the chemical composition of smaller particles, typically 10 - 50 microns, as well as larger areas on the surface.

FTIR analysis is used to:

1. Identify and characterize unknown materials (e.g., films, solids, powders, or liquids)
2. Identify contamination on or in a material (e.g., particles, fibers, powders, or liquids)
3. Identify additives after extraction from a polymer matrix
4. Identify oxidation, decomposition, or uncured monomers in failure

analysis investigations

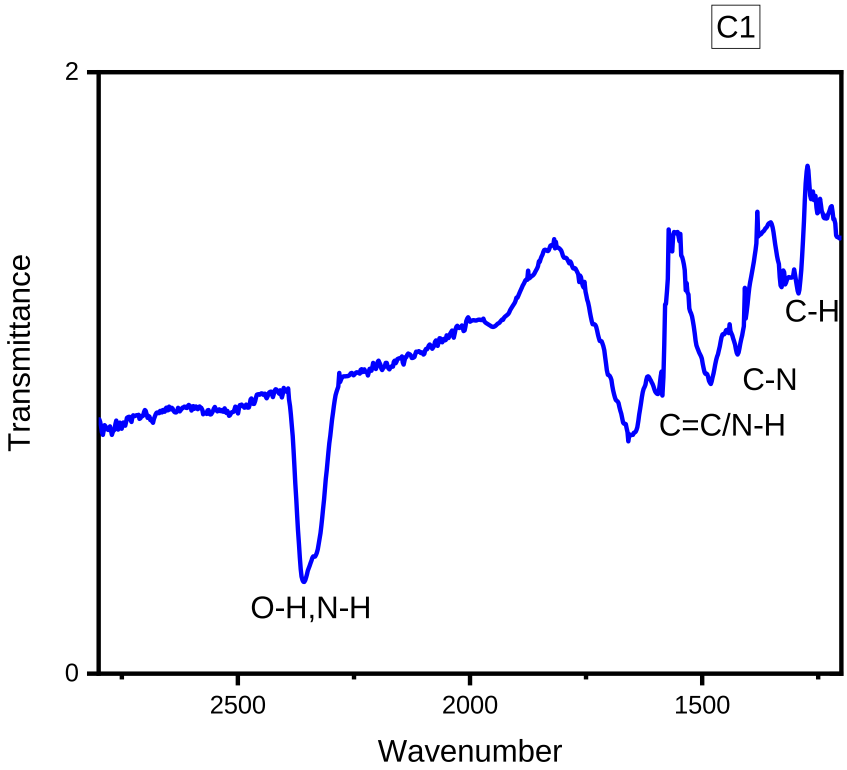

FIGURE 6.9: FTIR Spectroscopy of Carbon Dots

By analysing the FT-IR spectroscopy plot, we obtain a peak at 1653 cm−1 which reflects the presence of amide carbonyl, indicating successful conjugation between amines of piperazine and carboxyls of phthalic acid. The peaks at 1588 cm-1 and 1419 cm-1 are assigned to the bending vibration of C=C/N-H and C-N stretching. The peaks at 2357cm-1 and 1409 cm-1 indicate the stretching vibration and in plane bending vibration of O-H and N-H. The stretching and bending vibration of C-H is observed at 1293cm-1. All the above information proves the presence of hydroxyl, carboxyl and amino groups on the surface of carbon dots.

6.5 Images

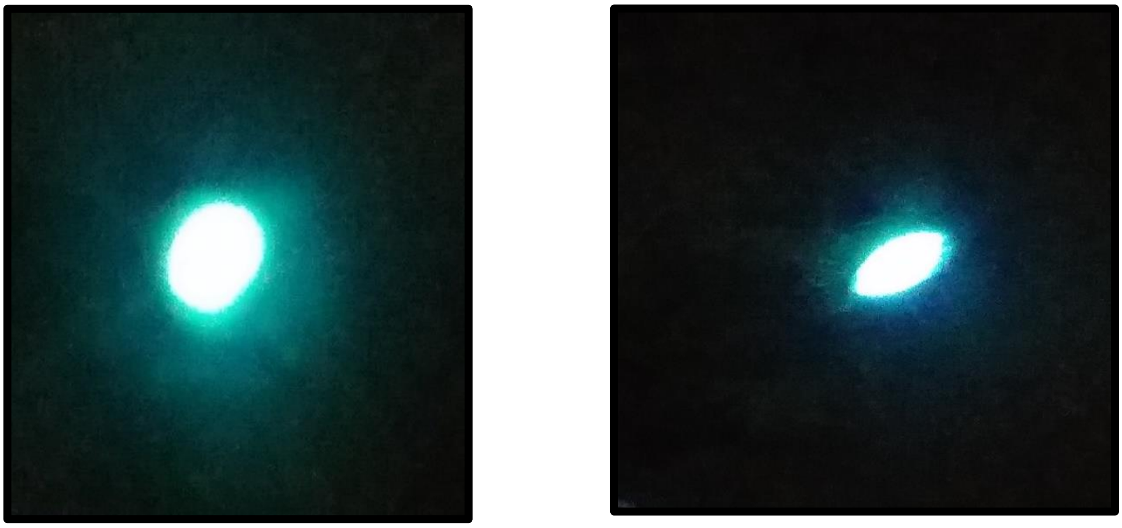

FIGURE 6.10: Fluorescent carbon dots

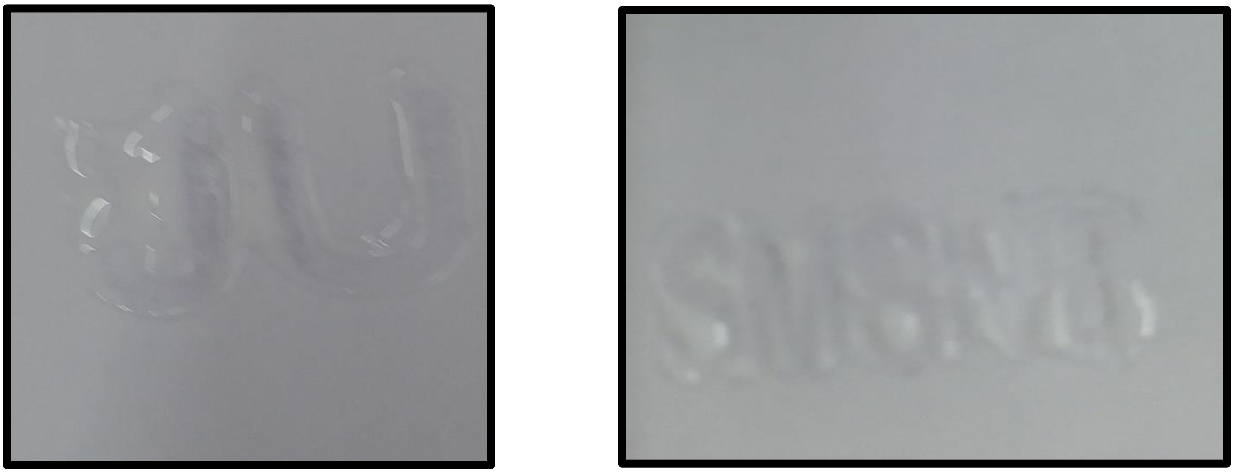

FIGURE 6.11: Security Ink under daylight

FIGURE 6.12: Fluorescent Security Ink under UV excitation

As shown in the above images, the transparent fluorescent ink in normal condition does not show any emission. However, when exposed to UV light source, it emits strong emission which can be utilised for protection against counterfeiting of important and confidential data. This ink has been tested on various substrates including paper, PVA film, glass slides etc.

6.6 References

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CHAPTER 7

CONCLUSION

&

FUTURE SCOPE

7.1 Conclusion

Carbon Dots were used in this study. Carbon Dots were successfully synthesized using a less time-consuming microwave synthesis procedure, and the products were modified subsequently. UV-Vis Spectroscopy was conducted as part of the characterisation process. Using PL analysis, we studied the excitation & emission spectra of Carbon Dots respectively and calculated the bandgap of the material. The Carbon Dots perform well as fluorescence emitter when exposed to UV light, as seen by their PL spectrum. Our sample produced strong green emission when exposed to UV light and thus it is was proven to be applicable for the development of anti-counterfeit/security inks.

7.2 Scope for Future work

Carbon dots (CDs), a zero-dimensional (0D) nanomaterial of the carbon family, have shown promising biomedical applications due to their ultra-small size, non-toxicity, biocompatibility, excellent photostability, tunable fluorescence, and water solubility, among other properties, capturing considerable attention in the biomedical field.

Despite substantial advances and demonstrated amazing benefits, the prospective bioimaging applications of GQDs have not yet been fully explored due to several unresolved obstacles. GQD research is still in its early stages. As a result, while there is a large development space for GQDs, there are still some issues that need to be addressed, such as low product yield and quantum yield, deficiencies in accurately controlling lateral dimensions as well as surface chemistry, the perplexing PL mechanism, narrow spectral coverage, a lack of tailor-made control of optical properties, and so on. Because of the advancements in grapheme, CDs, and even semiconductor quantum dots, there are several applications in biology, electronics, and other fields.