Fluorescent carbon dot aggregates for optoelectronic applications

M.Tech. Thesis

By

Dharmendra Kumar

DEPARTMENT OF METALLURGICAL ENGINEERING AND MATERIALS SCIENCE

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A THESIS

Submitted in partial fulfillment of the
requirements for the award of the degree
of
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by
Dharmendra Kumar

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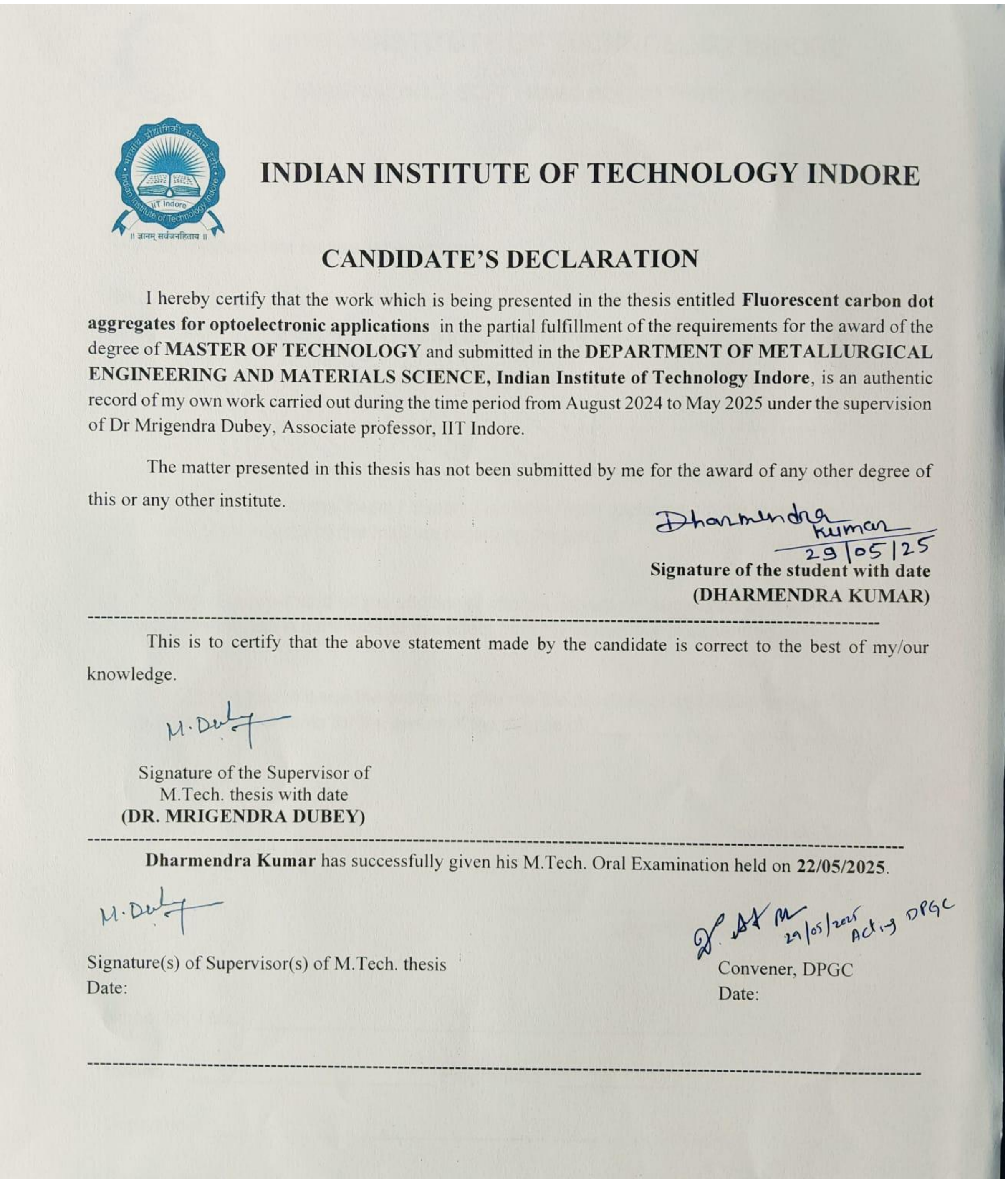

INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Fluorescent carbon dot aggregates for optoelectronic applications** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF TECHNOLOGY** and submitted in the **DEPARTMENT OF METALLURGICAL ENGINEERING AND MATERIALS SCIENCE, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from August 2024 to May 2025 under the supervision of Dr Mrigendra Dubey, Associate professor, IIT Indore.

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

Dharmendra Kumar
29/05/25
Signature of the student with date
(DHARMENDRA KUMAR)

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

M. Dubey

Signature of the Supervisor of
M.Tech. thesis with date
(DR. MRIGENDRA DUBEY)

Dharmendra Kumar has successfully given his M.Tech. Oral Examination held on **22/05/2025**.

M. Dubey

Signature(s) of Supervisor(s) of M.Tech. thesis
Date:

29/05/2025 Acting DPGC
Convener, DPGC
Date:

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DEDICATION

Dedicated to my Guide

My Parents

My teachers

My seniors

My Friends

Abstract

The study of Solid-state fluorescent carbon dot (CD) aggregates has been done in two part. In the part one for synthesis solvothermal and precipitation methods has been used with reactants 2,2′-dithiosalicylic acid with adenine or 4-aminobenzenethiol. The initially prepared CDs OD (from adenine) and GD (from 4-aminobenzenethiol) exhibited blue emission, but water treatment triggered a distinct shift to orange (ODA aggregates) and green (GDA aggregates) solid-state fluorescence. This emission switching stems from aggregation-induced emission (AIE) activated by water, with contact angle measurements confirming the hydrophobic surfaces of ODA and GDA. These ODA and GDA have been successfully applied in the fabrication of LEDs. In order to synthesize metal-doped CD aggregates with red fluorescence, synthesized by the same method using Nickel chloride, these hydrophobic aggregates demonstrated practical utility in fabricating fluorescent polymer covers for light-emitting diode (LED) devices, and the contact angle measurement of these CD aggregates is very significant. This type of hydrophobic contact angle may be used in metal corrosion protection applications. Additionally, their high fluorescence contrast enabled effective fingerprint detection, highlighting applications in forensic analysis and security systems.h

LIST OF PUBLICATIONS

1. Dharmendra Kumar, Bharat Kumar Sahu, Abul Kalam and Mrigendra Dubey, Color-tuneable hydrophobic carbon dots aggregates for LEDs applications, New J. Chem., 2025, **00**, 1-5**,** DOI https://doi.org/10.1039/D5NJ01351H

2. Metal-doped carbon dots aggregates and their applications (under *process*)

TABLE OF CONTENTS

Chapter 1: Introduction

Chapter 2

Applications

Chapter 3

Result and discussion

Chapter 4

LIST OF FIGURES

NOMENCLATURE

^{o} *Degree*

% *Percentage*

π *Pi*

θ *Theta*

List of Abbreviations

ODA – Orange carbon dots aggregates

GDA - Green carbon dots aggregates

CDs - Carbon dots

AIE – Aggregation-Induced Emission

ACQ – Aggregation Caused Quenching

PL - Photoluminescence

SSE – Solid State Emission

FTIR – Fourier transform Infrared
UV-Vis – Ultraviolet- Visible

PVDF – Polyvinylidene fluoride

MS- Mild Steel

Chapter 1

Introduction of carbon quantum dots

Introduction

1.1 Overview

Carbon dots (CDs) are a novel addition to the spherical, small nanoparticles of carbon with diameters below 10nm and rich oxygen-containing functional groups. The discovery of carbon dots was accidental, arising in the course of electrophoretic purification of single-walled carbon nanotubes (SWNTs) produced from arc-discharge soot. This process, described by Xu and co-workers in the Journal of the American Chemical Society, was originally designed to separate fluorescent fragments of nanotubes. Instead, it resulted in the discovery of new luminescent carbon particles. CDs were only later coined by sun et al. in 2006. This was a new area for research in nanotechnology and nanoscience. One major breakthrough in CDs research came with the development of a strategy for surface passivation to boost their fluorescence. From their nanoscale morphology, CDs show outstanding optical, chemical and physical properties. The non-toxic nature, biocompatibility of these carbon dots provide a big boom of application in the field of biomedical, cell imaging and sensing etc. They integrate very excellent electronic properties, making them superior to the light emission properties. These CDs are developed in two phases with the good water solubility and the other is it a fluorescent aggregated form so the unique properties have spurred extensive research activities with increasing interest in applying them in various technological domains.

1.2 Carbon Dots

CDs are nanoparticles with a quasi-spherical shape, and these nanoparticles are categorized based on their size and fluorescent properties. Due to its small size, they exhibit the quantum confinement effect. On their surfaces, CQDs are typically characterized by a variety of functional moieties, including -OH, -NH2, -COOH, etc.[1] These moieties are responsible for their exceptional water solubility, biocompatibility as well as hydrophilic and hydrophobic properties. In CQDs, functional moieties are organized in a network structure composed of oxygen and amino groups. Various chemical modifications can be performed on the surface of CQDs due to their numerous functional moieties. It is also possible to passivate CQD surfaces to enhance their physical properties and fluorescence, enabling interaction with different biologically active, inorganic, and organic materials. The surface state of CQDs can be precisely modified through hetroatom doping. Luminescence properties of CQDs are strongly influenced by their chemical structure. Several analytical techniques, such as Fourier transform infrared (FTIR) spectroscopy, ultraviolet visible (UV-vis) spectroscopy, among others have been employed to successfully characterize CQDs. These distinctive attributes confer a competitive advantage to CQDs over other carbon-based nanomaterials. CDs are investigated in four classes, namely graphene quantum dots (GQDs), carbon quantum dots (CQDs), carbon nanodots (CNDs), and carbonized polymer dots (CPDs).[5,6]

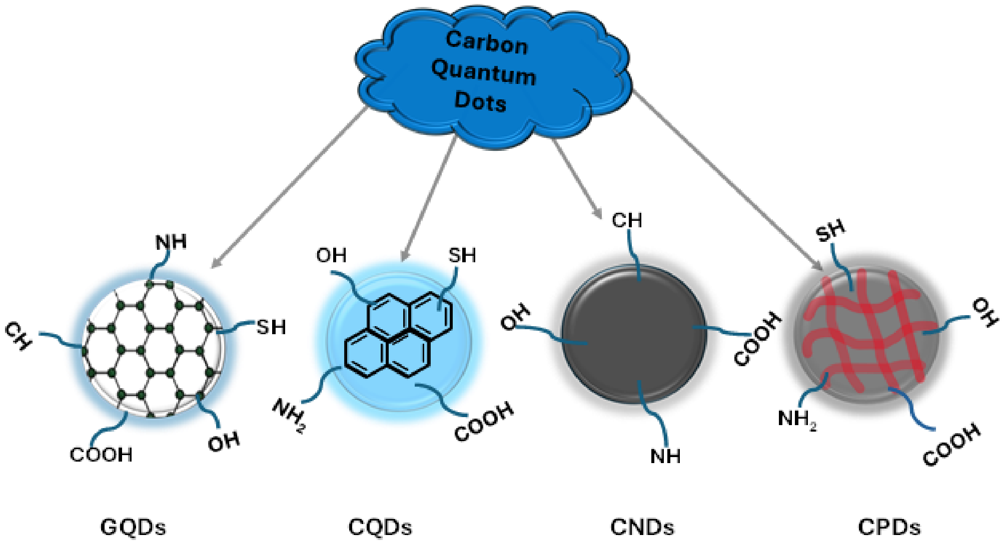

Fig. 1.1 Representation of existing carbon dots: graphene quantum dots, carbon quantum dots, carbon nano dots, and carbon polymer dots.

Photolumenescence

Carbon dots (CDs) are increasingly showing great potential as excellent photoluminescence (PL) materials that are useful for various applications. Optical characteristics such as color emissions in the CDs significantly depend on their composition, morphology, and synthesis procedure. Although they hold great promise, the general application of CDs is generally restricted by challenges in their synthesis control and the still-poorly understood PL mechanisms. More specifically, the PL characteristics of carbon dots are primarily due to quantum confinement effects and other surface-related effects.[7] The emission properties are influenced by surface functional groups, structural defects, doped heteroatoms, and the edge configuration of the particles. Still, however, the underlying mechanism for their luminescence is not totally understood. A majority of reported CDs have shown blue or green luminescence and follow general excitation-dependent emission characteristics. This tends to be because they have varying sizes and surface groups, and introducing heterogeneity becomes a challenge. To counter this and expand CDs' emission bands, the new work has concerned itself with how to better engineer synthesis. By meticulously adjusting parameters such as particle size, surface chemistry, and the surrounding environment (e.g., the type of solvent, pH, and concentration), scientists hope to create CDs with stable and controllable emissions over a wider color range. This achievement brings new opportunities for them to be used in applications ranging from bioimaging to light-emitting diodes (LEDs) and chemical sensors. The photoluminescence (PL) of carbon dots (CDs) may arise from various emissive states: core states, edge states, and surface states. Core state emission is mostly related to the intrinsic carbon core and is affected by the quantum confinement effect, often yielding blue emission. Edge state emission results from the localized states at the edge of sp^2 carbon domains, usually influenced by defects and heteroatom doping, to give rise to tunable emissions. Surface state emission is a result of different functional groups and chemical bonding on the surface of CDs that can trap excited electrons and lead to emission in a wide range of wavelengths, tending to give excitation-dependent behavior.[8,9]

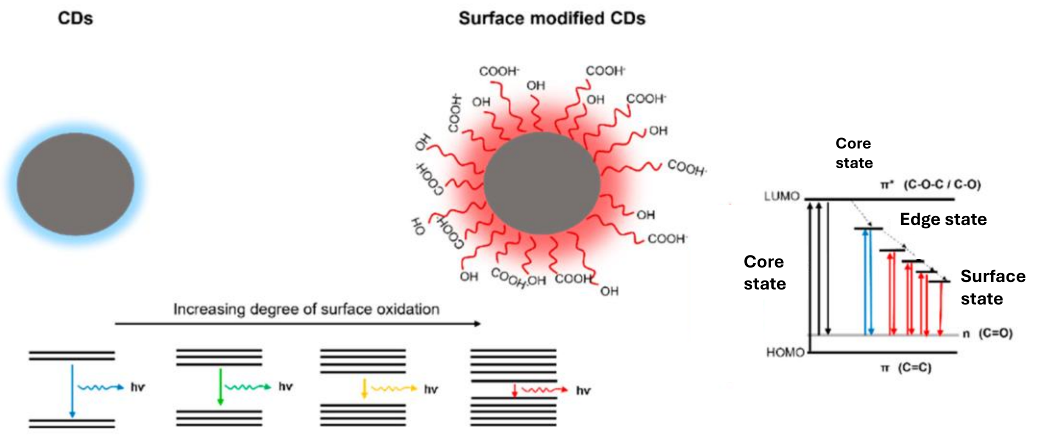

Fig. 1.2 The demonstration of photoluminescence from different core state, edge state, and surface state, as well as the effect of band gap on luminescent properties of carbon dots.

1.4 Hydrophobicity

Hydrophobicity is the capacity of a surface to reject water, generally indicated by a contact angle with water more than 90°. Hydrophobicity originates from low surface energy and little interaction between the surface and water molecules. Surfaces with nonpolar functional groups like alkyl or fluorinated chains lower the affinity of water to spread, leading to droplet formation and poor wetting. In addition, surface roughness and hierarchical structures can enhance hydrophobic behavior by air entrapment and low solid-liquid contact, as postulated by the Wenzel and Cassie-Baxter models. Hydrophobic materials are critical in a wide range of applications, such as anti-corrosion coatings, self-cleaning surfaces, and water-resistant films. Carbon dots (CDs) are a family of fluorescent carbon-based nanomaterials that have attracted immense interest owing to their tunable optical and surface properties. When engineered into solid-state carbon dots (SS-CDs), the materials become stable in fluorescence even without the presence of a solvent, thereby circumventing the usual problem of aggregation-caused quenching (ACQ). SS-CDs not only preserve their photoluminescence in solid form but also present increased structural stability and better surface functionality. For example, studies have investigated the aggregation-induced emission (AIE) behavior of SS-CDs prepared through a one-step solvothermal process with DTSA and acetic acid. The presence of disulfide bonds within the structure is responsible for restricted water compatibility and increases the hydrophobic nature of the resultant SS-CDs, making them appropriate for versatile applications where solvent-free fluorescence is demanded.[10]

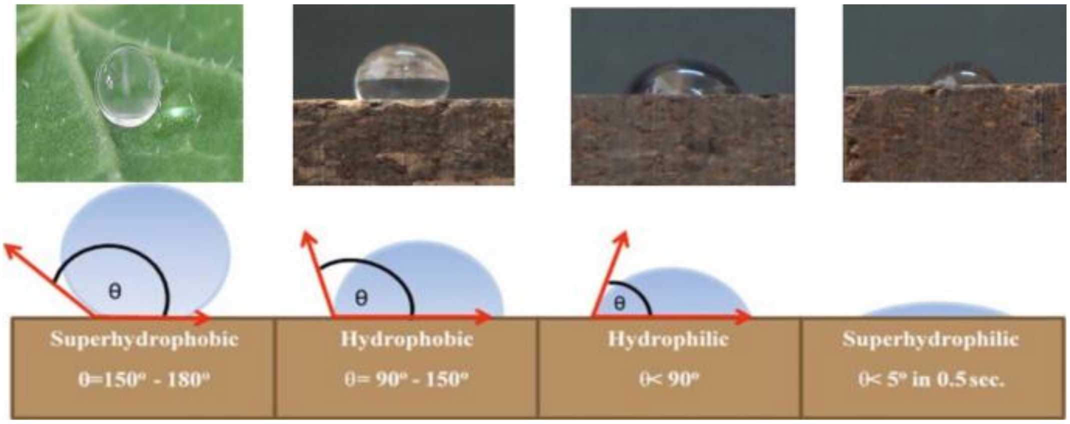

Fig. 1.3 Classification of hydrophilic and hydrophobic nature of surfaces based on contact angle.

1.5 Synthesis approaches of carbon dots

Numerous techniques have been developed to synthesize CDs after their discovery. Nonetheless, the synthesis strategies of CDs can be mainly classified into “top-down” and “bottom-up” based on the sources of the substrate and the reaction method.

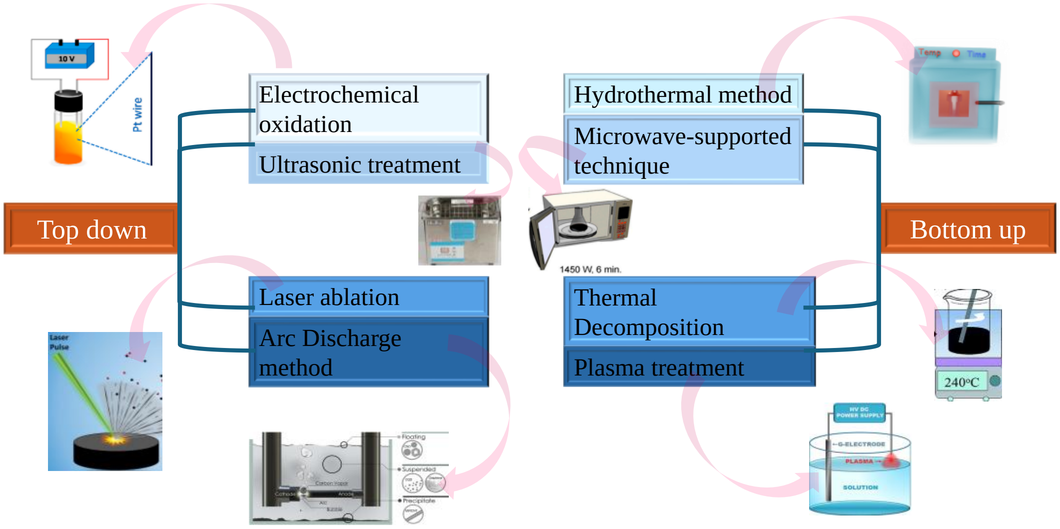

Fig. 1.4 The schematic representation of synthesis processes of carbon dots from different approaches: top-down approach and bottom-up approach.

1.6 Applications of CDs

The area of fluorescent carbon dots is growing very fast in the field of materials science, providing scientists with new challenges to create new materials with unique properties. By examining different synthesis routes, performing extensive characterization, and studying various applications, researchers can promote innovation in this field. The increasing interest stimulates deeper investigation into fabrication processes, better comprehension of the underlying mechanisms governing their behavior, and the identification of new useful applications for these promising nanomaterials.

Fingerprint detection

Latent fingerprints (LFPs), deposited on surfaces following contact with fingers or hands, are an important physical evidence in forensic science and personal identification. The prints are usually not easily visible to the naked eye because of their low optical contrast. Therefore, imaging methods for visualizing LFPs are important in identifying individuals. Conventional image techniques, including solution-based spraying, are plagued by signal decay and progressive loss of detail. Conversely, powder-based techniques—albeit still in their early stages—have the benefit of yielding sharper images with stable long-term behavior and thus hold promise for realistic forensic applications. Fluorescent carbon dots (CDs), which possess high luminescence, simple synthesis, and favorable biocompatibility, have excellent prospects in improving LFP detection. Their monodispersity and uniform size make them useful for enhanced sensitivity and selectivity in imaging. The high intensity of fluorescence in CDs also increases the visual contrast of fingerprints, making them more recognizable and credible for forensic examination.[11]

Photovoltaic applications

Luminescent carbon dots (CDs) have great promise in solid-state lighting and optoelectronic devices. They can be efficiently employed as phosphors in LEDs, as the emissive layer in QLEDs, and as gain media or phosphor materials for laser devices (LDs). Their photostability along with simplicity in integration makes them good applicants for future lighting and display technologies.[12]

Visible light communication

Visible light communication (VLC) is a cutting-edge technology that uses light for high-speed data transmission, making it possible to have the idea of "where there's light, there's internet" with LED or laser lighting. In essence, VLC integrates lighting and wireless communication. This method has numerous benefits, including high efficiency in transmission, excellent immunity to interference, lack of electromagnetic radiation, improved safety, minimum environmental impact, and affordability. It also enables ultra-low energy communication and minimizes electromagnetic signal leakage risk that is common in radio-based systems. Consequently, VLC is attracting more and more interest in wireless communication. One of the challenges in VLC is the application of conventional rare-earth-based phosphors with prolonged fluorescence lifetimes. This constrains the modulation bandwidth and hence the data transmission rate. Conversely, materials with reduced fluorescence lifetimes facilitate quicker response times and higher bandwidth compatibility with the lighting source and hence are better suited for VLC systems. Carbon dots (CDs) with their short fluorescence lifetimes are exemplary materials for VLC systems on account of their quick response and ability to increase communication speed.[13]

Security purpose inks

Carbon dots (CDs) exhibit excellent optical properties like excitation-dependent photoluminescence, intense and tunable fluorescence, high quantum yield, and superior photostability, which make them highly potential materials for fluorescent security printing. Such characteristics allow their use in sophisticated anti-counterfeiting and data-security technologies. Apart from their optical benefits, CDs are also appreciated for their simplicity in synthesis, scalability, low cost of production, favorable biocompatibility, and low toxicity. Their wide coordination versatility, chemical stability, solubility in water, and favorable dispersibility in aqueous systems further endorse their incorporation into various printing formulations. These features make CDs very suitable for new research in the area of security printing materials. Drawing on this background, the second part identifies current advances in the synthesis and use of fluorescent CDs as security inks with particular emphasis on anti-counterfeiting and data storage applications.[14]

Energy storage

CQDs used to have very limited applications, but once they were found to possess a range of peculiar properties, now they are more sought after than ever. Applications of CQDs in different energy-related fields super-capacitors, batteries, water splitting, and photo detectors discussed in this section here.

1.7 Literature Review

Carbon dots (CDs) are nanoscale particles that are most commonly synthesized via an aggregation-induced crosslinking and carbonization process involving small organic molecules or polymers. Most of their photoluminescence (PL) is due to the confinement enhancement effect, which enhances their optical performance. CDs are particularly appreciated for their excellent optical properties, good biocompatibility, low cost, easy accessibility, and environmental safety. These attributes make them extremely viable for numerous applications, such as bioimaging, optical sensing, solar energy conversion, and photocatalysis. In spite of these benefits, a key challenge to their development is aggregation-caused quenching (ACQ). Although CDs exhibit intense fluorescence in solution form, their luminescence tends to be greatly reduced in the solid state. Such a decrease in emission is typically brought about by mechanisms such as internal Förster resonance energy transfer and non-radiative pathways caused by π–π stacking or aggregation of highly packed particles. Consequently, this problem restricts the use of CDs in practical applications of solid-state emission technologies. In an attempt to resolve the issue of aggregation-caused quenching (ACQ) in carbon dots (CDs), there has been significant development over the last decade. Pan and co-workers were, in 2011, amongst the first researchers to successfully create carbon dot thin films with blue emission, which was an early demonstration of solid-state emissive (SSE) carbon dots.[15] Drawing on this, Liu and colleagues published embedding CDs in solid macrostructures in 2012. The materials showed not only intense luminescence in the solid state but also remarkable mechanical and thermal stability, which unlocked new possibilities for SSE CDs in a wide range of applications.[16]

The early synthesis of SSE CDs depended highly on embedding the dots in solid matrices, which typically entailed complicated processes, high expenses, and lengthy processing times. To overcome these limitations, Ding and colleagues have devised a scalable, low-cost, one-pot synthesis method that could directly prepare SSE CDs—a crucial breakthrough for practical applications.[13] Chen and his group further advanced the process to synthesize SSE CDs with yellow-green emission through polyvinyl alcohol as a carbon source. Even with these developments, early SSE CDs mostly emitted in the shorter wavelength ranges, including blue, green, or yellow, creating a gap for materials that have broader or acceptable emission profiles. In 2017, Liu and others made a significant advance by creating solid-state emissive (SSE) organosilane functionalized carbon dots that emitted in the red region, successfully pushing the emission spectrum beyond previous constraints. Following this breakthrough, Xu and colleagues extended the horizon further by demonstrating near-infrared (NIR) emission of SSE carbon dots with an extraordinary photoluminescence quantum yield (PLQY) of 67.7%.[17] These advances have significantly broadened the functional scope and use prospects of SSE CDs. Consequently, this field has attracted vast research interest in recent times with many studies joining the expanding pool of research with the different synthesis methodologies, the one-pot solvothermal method has been particularly beneficial. It possesses a myriad of advantages, most notably relatively low processing temperatures, which promote environmental sustainability and cost-effectiveness. It also facilitates the employment of the wide range of organic compounds as precursors, which are generally more available and cost-effective than other carbon sources. Consequently, this approach facilitates the production of a wider variety of carbon-based nanomaterials and encourages a greener and more efficient route to SSE carbon dot preparation. Historically, aggregation of the fluorescent molecules has been linked with a reduction in their luminescence intensity, described as aggregation-caused quenching (ACQ). Conversely, an opposite behavior termed as aggregation-induced emission (AIE) has recently become the focus of considerable interest see in fig. 1.5. Fluorescence is enhanced in AIE-active materials upon aggregation of molecules. This is because, when in the dispersed state, the fluorescent molecules tend to have free rotation of surface groups around internal bonds, resulting in non-radiative dissipation of the absorbed light. Therefore, not much energy is radiated as light. Upon aggregation, the intramolecular motions of these molecules are significantly hindered, which

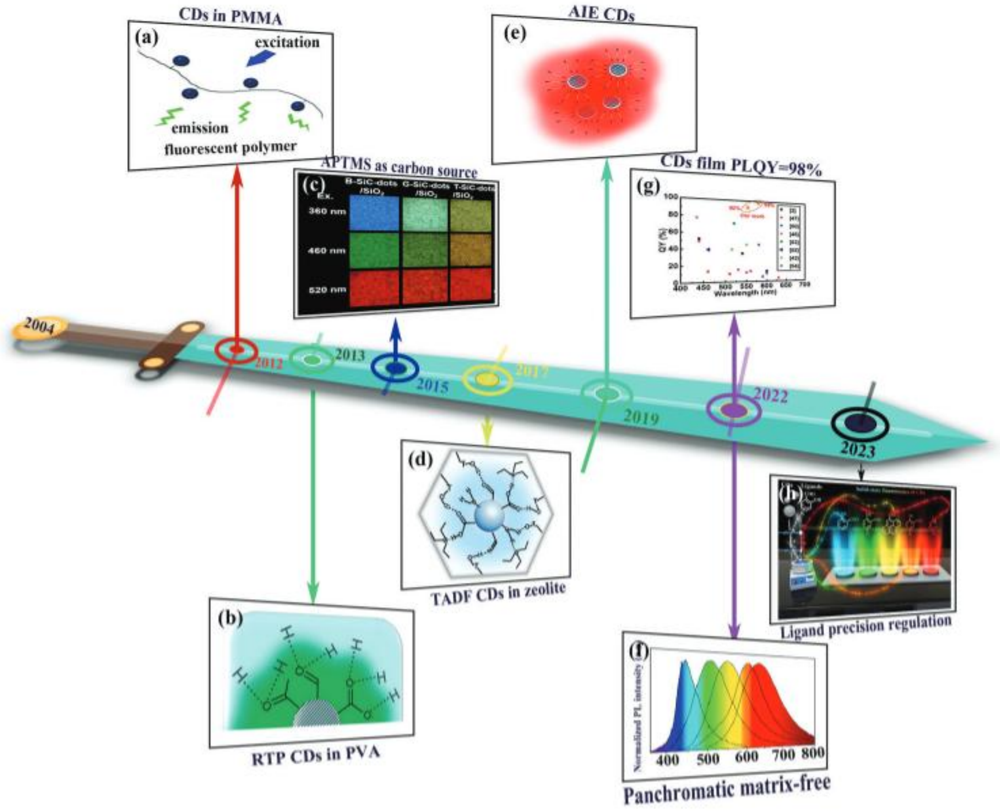

Fig. 1.5 The year-wise progress in the solid state carbon dots representation from 2004.

decreases the energy loss by internal conversion and increases the radiative emission. Inspired by this exceptional AIE phenomenon of the typical fluorophores, scientists have begun to investigate if carbon dots (C-dots), especially those synthesized under solid-state emission (SSE) conditions, will also display AIE properties. Pioneering work in this research direction was reported by Liu and co-workers, who synthesized the C-dots from melamine and DTSA under a one-pot solvothermal process. These C-dots had blue photoluminescence in solution and red emission in the solid state. Enhancement of emission in the aggregated form was due to hindered rotation of disulfide-bearing surface groups, and hydrophobicity of the particles was associated with structural features such as pyridinic and epoxy functionalities on their heterocyclic surfaces see in fig. 1.6.

After this revelation, numerous researchers have explored SSE C-dots with AIE-like luminescence. For instance, Zhang et al. synthesized C-dots that exhibited a characteristic AIE behavior, showing enhanced yellow fluorescence upon increased concentration of the dispersion.[18]

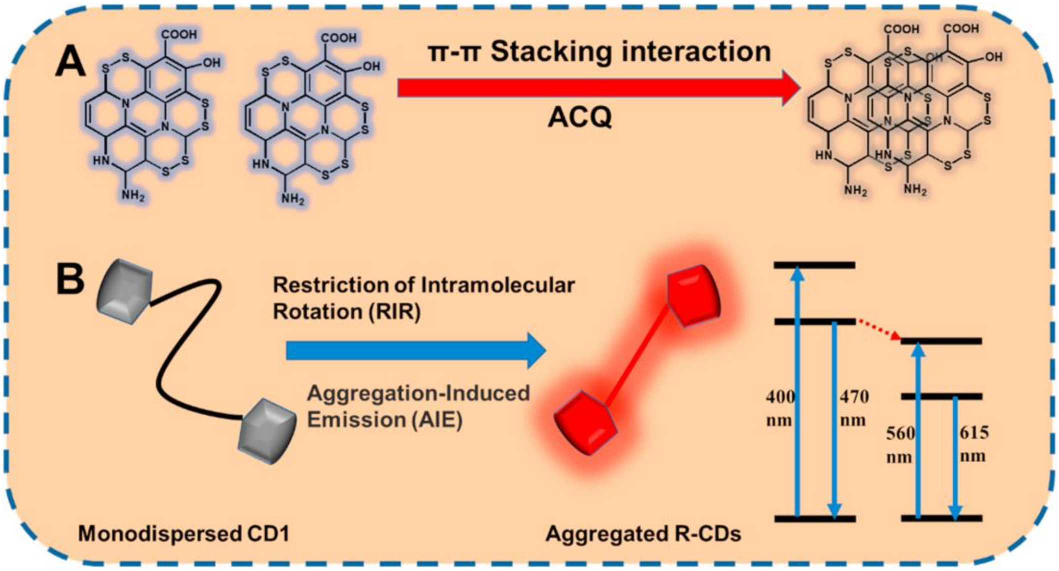

Fig. 1.6 (A) demonstration of the π-π stacking with the ACQ effect in the carbon dots and (B) demonstrates the restriction of intramolecular rotation after aggregation of blue dispersive particles.

Likewise, Yin and colleagues prepared hydrophobic carbon dots from straightforward organic precursors such as aliphatic amines and aldehydes, each bearing only a single functional group. This research extended the synthetic scope of carbon dots by showing that multifunctional precursors aren't necessarily required to produce desirable photophysical features.[19] Recently, water-soluble carbon dots that exhibit intense yellow fluorescence and aggregation-induced emission (AIE) character were developed by researchers, Enhanced emission was attributed to the inhibited motion of surface-attached piperazine groups that decreased nonradiative energy dissipation.

New methods of developing hydrophilic carbon dots with efficient solid-state luminescence were offered by this work.[20] The same study also explored the use of cyclodextrins with different surface properties. Hydrophobic cyclodextrins were shown to be suitable for forming solid luminescent materials that could be shaped into various forms, making them useful in optical applications. In addition, their potential use as components in LED lighting was demonstrated. Even with advancement in synthesis, there are still some hindrances. Although direct routes to solid-state emissive carbon dots have made the process easier, there are still issues like poor dispersion and poor emission efficiency. In addition, these processes tend to need careful choice of both carbon precursors and dispersing agents. Relative to classical carbon dots, fine-tuning the optical properties of solid-state emissive dots is still an emerging area, and it is challenging to attain targeted performance. By contrast, AIE-active carbon dots provide a very promising solution. These dots are synthesized from well-selected molecular precursors and inherently become more fluorescent as they form aggregates. This characteristic distinguishes them from common carbon dots and provides new avenues for enhancing solid-state fluorescence performance. With respect to applied usage, an example is the research by Xiang-yang Dong's group, who synthesized red-emitting carbon dots from starch. The dots were successfully used in fingerprint detection with a powder-dusting process. The fact that they were hydrophilic enabled them to adhere to fingerprints residues, thereby making the patterns visible under appropriate lighting.[21]

Light-emitting diodes (LEDs) are viewed as the latest generation of green and energy-conserving lighting technologies. LEDs are used broadly because they consume less power, have a long lifespan, produce minimal heat, and are green-friendly. LEDs are now ubiquitous in many aspects of everyday life. LED color conversion is generally based on phosphors, semiconductor quantum dots, and fluorescent materials. However, there are each of their drawbacks. Phosphors tend to crystallize in large aggregates, which compromise their color converting efficiency.[22] Semiconductor quantum dots, though very efficient, tend to be composed of heavy metals such as cadmium or chromium, which are harmful to the environment and human health.[20] Conventional fluorescent powders also need high calcination temperatures, typically over 1000 °C, and rely on rare earth elements, thus being less environmentally friendly. Carbon dots (CDs) are stepping up to the plate as very viable alternatives. They are biocompatible and eco-friendly, and they can also be synthesized with low-cost, simple, and green processes. For example, it was shown in a study that the solvent in a synthesis with tartaric acid and triammonium citrate could be modified to provide multicolor fluorescent CDs. They were incorporated into white-light LEDs successfully. Another strategy entailed the creation of warm white LEDs based on phosphors obtained from microwave-assisted pyrolysis of sodium silicate, subsequently encapsulated in polyvinyl alcohol (PVA) films. Even with these developments, the majority of CDs are utilized in solution form. When they are converted to solid-state, a lot of CDs are subject to aggregation-caused quenching (ACQ), which immensely reduces their fluorescence. Furthermore, CDs tend to exhibit poor compatibility with epoxy resins, which are typically employed in LED encapsulation. Another challenge is that most known LED devices using CDs produce warm white light, and single-color LEDs, especially those with high purity and long wavelengths, are far less studied. This has generated more interest in AIE-type carbon dots. These materials not only provide high quantum yields but also retain or even increase their fluorescence in solid state, overcoming the drawbacks of ACQ. Thus, the construction of AIE-active CDs with high solid-state luminescence and color purity offers a promising route for future LED applications. The goal of high quantum efficiency and prevention of fluorescence quenching in the solid state remains key to the further development of carbon dot-based light conversion technologies.[23]

In this research, we synthesized highly fluorescent and hydrophobic solid state carbon dots through one pot solvothermal method, which was utilized in orange and green emissive LEDs fabrication. CDs further synthesized used on the fingerprint detection.

1.8 Aggregation-induced emission

Carbon dots (CDs) present a straightforward method to tune their emission range and quantum yield (QY) by adjusting the concentration. For instance, Wang et al. used citric acid and ammonia in a microwave to synthesize CDs with concentration-dependent photoluminescence (PL) behavior. As the concentration increased, the PL emission exhibited a red shift, moving from 450 nm (0.78 mg/ml N-GQDs) to 523, 550, and then 600 nm. The synthesized N-CDs showed similar size distribution and surface characteristics across all concentrations, suggesting that these factors had minimal impact on the observed red shift. Therefore, the emission red shift is attributed to self-absorption, a consequence of the decreasing distance between N-CDs. In one study, researchers noticed that carbon dots showed a change in their light emission from blue to green as their concentration increased in water. This color change was believed to result from the particles coming closer together, which caused a shift in how electrons were distributed due to the interaction of surface groups. The blue emission was related to regions in the carbon dots that had sp^2 bonding. In the solid state, carbon dots emitted yellow light, which is likely due to the dense packing of particles that increases the extent of conjugation and reduces the energy gap between electronic levels. The effect of carbon dot (CD) aggregation on emission properties, including quenching, enhancement, and multicolour emission, is a subject of considerable research. As an illustration, Wang et al. demonstrated aggregation-induced quenching (AIQ) of CDs by Co^{2+} ions, which has potential applications in detecting apoptotic markers. Conversely, Lv et al. discovered that Cu^{2+} induced aggregation-induced emission enhancement (AIEE), a phenomenon that contrasts with the more typical AIQ of CDs. With increasing Cu^{2+} concentration, a color shift from light yellow to dark yellow was observed, which was attributed to increased efficiency of n-π^* transitions. In one study, red-emitting CDs exhibited pressure-induced aggregation, which resulted in enhanced CD emission. Theoretical investigations have also indicated that self-assembly and the stacking of conjugated domains within CDs leads to emission enhancement. Chen et al. reported aggregation-induced emission transformation of GQDs in 2012. For example, Wang and colleagues observed that carbon dots experienced aggregation-induced quenching (AIQ) in the presence of Co^{2+} ions, suggesting their usefulness in identifying apoptotic signals. In contrast, research by Lv and co-workers showed that Cu^{2+} ions could trigger aggregation-induced emission enhancement (AIEE), which is the opposite of the commonly seen quenching behavior in carbon dots. As the concentration of Cu^{2+} increased, the emission color changed from pale yellow to deep yellow, likely due to a greater contribution from $n–\pi^*$ electronic transitions. Another study found that red-emitting carbon dots displayed enhanced luminescence when pressure caused them to aggregate. Computational studies have further supported that the stacking and self-organization of conjugated regions within carbon dots can amplify their emission. Additionally, in 2012, Chen and team documented an emission shift caused by aggregation in graphene quantum dots.Edge carboxylic groups can also inhibit π-π stacking which can lead to self-assembly into J type aggregation. Based on particle aggregation, Zhang et al. fabricated carbon dots (CDs) exhibiting multicolour emission that depended on concentration. The emission displayed a red shift with increased aggregation, a phenomenon that can be described by quantum confinement effects (QCE) in aggregates. As a function of concentration, the red shift was favoured by a narrowing band gap and the splitting of excited energy levels. Studying how carbon dot emission changes with concentration can reveal important details about their electron transition behavior, especially at low concentrations. In one experiment, Wang and co-researchers created carbon dots that displayed a color shift in their emission—from blue to orange—as the concentration increased. Their analysis showed that this shift was linked to interactions between surface groups on the particles, which led to the creation of new energy states at lower levels. These interactions caused the emission to move toward longer wavelengths. The red shift was ultimately explained by electron transfer occurring within the aggregated structures, where electrons moved from smaller to larger carbon dots. Yang and co-workers developed hydrophobic carbon dots (H-CDs) that emitted blue light when well-dispersed but shifted to red emission upon aggregation. In aqueous environments, the aggregation of these H-CDs led to quenching of blue fluorescence, which was attributed to π–π interactions among the carbon cores. At the same time, restricted motion around the sulfur-containing bonds gave rise to red emission. This change in emission was reversible in solution, and similar red emission was noted in the solid state due to continued aggregation. Additionally, the emission behavior of H-CDs varied depending on the solvent: they emitted blue light in solvents like acetic acid and ethanol, while both blue and red emissions were observed in DMF, indicating the coexistence of dispersed particles and aggregates. Su and colleagues also reported related findings. In a recent study, researchers developed two types of carbon dots (CDs)—one exhibiting concentration-dependent emission and another, modified with zirconium (ZrCDs), showing concentration-independent behavior. For the undoped CDs, increasing the concentration caused a red shift in emission, which was attributed to factors such as aggregation, self-absorption, and the inner filter effect. However, the emission of ZrCDs remained stable across concentrations, as the presence of zirconium complexes on their surface effectively prevented aggregation, maintaining a consistent band gap. Despite this, both CDs and ZrCDs experienced fluorescence quenching in the solid state Building on this, Nayak and collaborators synthesized red-emitting, water-soluble CDs that displayed yellow fluorescence upon aggregation. Their emission behavior also varied with pH. Under acidic conditions, the fluorescence intensity decreased due to protonation of amide groups. In contrast, at high pH levels, hydrolysis of these amide groups led to the breakdown of aggregates and release of individual CD particles containing hydroxyl, carboxyl, and amine groups, resulting in a blue shift in emission. Interestingly, the yellow emission under acidic conditions was reversible, whereas the blue emission observed in alkaline environments was not. [24]

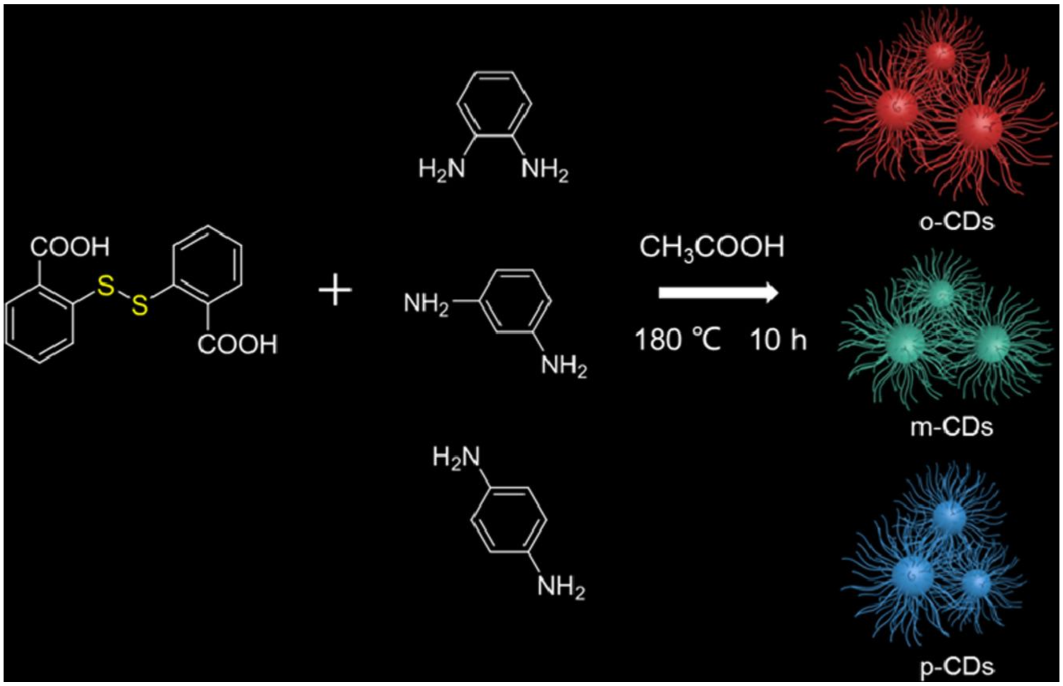

Fig 1.7 Production of hydrophobic carbon dots with red, green and blue aggregation-induced emission by using DTSA and o-phenylenediamine, m-phenylenediamine, and p-phenylenediamine.

Research gap

While carbon quantum dots (CDs) have garnered significant interest because of their extensive applications, there is a significant research gap involving the specific types of multichromatic, superhydrophobic, and fluorescent CDs, particularly in their dual format. With the majority of previous publications focusing on either hydrophobicity or fluorescence alone, there is limited activity towards coupling both properties into one device system. This offers a special prospect of broadening the scientific basis and real-world potential of such multistep materials.

Thus far, scientific investigations have essentially confined hydrophobic and fluorescent CDs into their own respective fields. The combination of multicolor emission and efficient water repellency within one carbon dot material has only been studied to the surface. The attainment of this coordination necessitates the creation of surface chemistry and synthesis strategy that is customized to produce substances that display both intense multicolor photoluminescence and stable hydrophobicity. Thus, synthesis and investigation of superhydrophobic, fluorescent, multichromatic CDs represent an unexplored area with tremendous promise.

Current literature also lacks detailed investigation into the structural, morphological, and optical characteristics of such complex carbon dots. Advanced analytical methods are needed to optimize their synthesis and fully understand their properties. Comprehensive characterization—including surface functionality, particle size, emission behavior, and water-repellent features—is essential for tailoring these materials for real-world use.

Additionally, practical uses of these multifunctional CDs are in their infancy. While interest in using them for fingerprint identification and incorporation into superhydrophobic coatings is increasing, few studies have investigated their efficiency, sensitivity, and scalability for such applications. Novel fabrication techniques and improved material performance must make these uses more viable on a commercial scale.

Apart from these applications, the possibilities of multichromatic superhydrophobic fluorescent CDs in biomedicine and the environment have been explored little. Their potential in pollutant detection, water quality assessment, targeted imaging, and drug delivery systems holds promising prospects. Nevertheless, knowing how they behave under various biological and environmental conditions is important before one can achieve such applications.

Overall, the research gaps present today illustrate the urgency of further exploring multichromatic superhydrophobic fluorescent carbon dots. Such progress would bring scientific discovery and technological advancements in fields like forensic science, protective coatings, environmental monitoring, and biomedical diagnostics. Further research into their synthesis, characterization, and solid-state performance will enable new avenues to apply carbon dots in numerous high-impact areas.

Although carbon dots have exhibited excellent optical performance appropriate for light-emitting diode (LED) devices—e.g., photoluminescence tunability, high photostability, and eco-friendliness—their application into efficient LED devices remains a challenging issue. One main limitation is the low solid-state emission of the majority of CDs based on aggregation-caused quenching (ACQ), lowering their fluorescence when incorporated into solid matrices such as polymers or epoxy resins often employed in LED packaging. While aggregation-induced emission (AIE)-type CDs have, to some extent, overcome this problem, the area as yet lacks systematic synthesis protocols for making AIE-CDs with high quantum yield, wide color tunability, and solid-state long-term stability. Moreover, the majority of CD-based LEDs have been blue or white emissions, with very limited study of high-purity red, green, or near-infrared emissions, which are needed for full-color displays and specific lightings. There is also insufficient deep understanding of the host-matrix interaction mechanisms with CDs, which is a critical factor towards optimizing energy transfer, emission efficiency, and device stability. These gaps are addressed by a multidisciplinary strategy that integrates materials chemistry, device engineering, and sophisticated photophysical measurements in order to facilitate reliable application of CDs in multicolor, high-performance, and stable LED devices.

Chapter 2

Color-tuneable hydrophobic carbon dots aggregates for LEDs applications

2.1 Materials and Methods:

Methanol was purchased from Advent Chembio Pvt. Ltd, Navi Mumbai India. Acetic acid purchased from Sisco Research Laboratories Pvt. Ltd. Mumbai Maharashtra. DTSA was purchased from Sigma-Aldrich, Mumbai (India). Adenine was purchased from Sisco Research Laboratories Pvt. Ltd. Mumbai Maharashtra, India and 4-Aminobenzenethiol purchased from TCI Pvt. Ltd. Concentrated H_2SO_4, DMSO, Ethanol were obtained from Qualikems Fine Chem Pvt. Ltd., Vadodara (India). All the reagents were used as received without further purification. FT-IR data were acquired using spectrum two PerkinElmer ATR FT-IR spectrometer. UV-vis study was done on UV2600 Schimazdu spectrophotometer. PXRD data was obtained from Empyrean Malvern Panalytical instrument (Cu-Kα radiation) between angle $2\theta = 3\text{-}80^o$. Photoluminescence spectra were obtained from perkinElmer fluorescence spectrometer (FL8500). FE-SEM images were procured using JEOL-7610 F Plus. The contact angle measured from Kruss GmbH DSA-25E drop shape analyzer.

2.2 Synthesis and device preparation

Synthesis of ODA

In the preparation of CDs 275mg of DTSA and 108mg of Adenine was dissolved in 20mL of acetic acid. The solution was sonicated for 20 minutes, after transferring the uniform mix to the Teflon-lined autoclave, it was heated at 180°C for 10 hours. Obtained liquid was centrifuged at 10000rpm for 20 minutes and large particles separated after the solution was filtered using a 0.22μm syringe filter. 200mL boiling DI water was added to the solution and aggregated CD powder was called ODA.

Synthesis of GDA

For green CDs, 275mg of DTSA and 100mg p-amino benzene thiol were taken with the same procedure but there is no need for hot water here normal DI water is enough, in the synthesis of ODA hot water is used for preventing much aggregation, and fluorescence result.

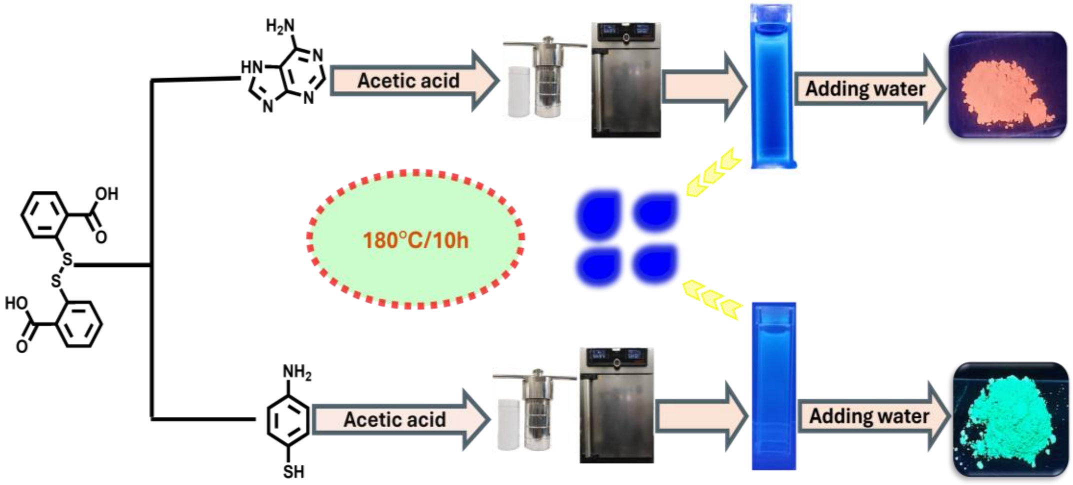

Fig. 1.8 Typical representation of the synthesis process of the carbon dots and their aggregation form of ODA and GDA.

2.3 Result and discussion

The aim of this work was to utilize nitrogen-based precursors, carbon core precursors, and disulfide bonds in the synthesis of carbon dots (CDs), with a particular focus on introducing nitrogen and sulfur into the structure via their respective precursors. These heteroatoms play a crucial role in enhancing the fluorescence properties of the CDs. The disulfide bond, in particular, facilitates aggregation through interactions with nitrogen and sulfur functionalities, contributing significantly to the overall photoluminescence behavior.

A schematic representation of the synthesis process has been provided in the preceding chapter. Through this method, both ODA and GDA were successfully synthesized, exhibiting strong fluorescent properties. The synthesized materials were thoroughly characterized using a range of analytical techniques, including Fourier-transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and various spectrophotometric methods.

The incorporation of benzene rings into the carbon dot structure exerted a notable influence on their properties. Aromatic interactions and π–π stacking between benzene units contributed to a more ordered carbon structure, which in turn enhanced the optical characteristics of the resulting CDs. This structural organization is considered a key factor in improving the photophysical performance of the materials.

In this study, various characterization techniques were employed to analyze both the structure and functional properties of the synthesized carbon dots. XRD and FESEM were used to investigate the crystalline structure and surface morphology, respectively. For optical property evaluation, UV–visible absorption and photoluminescence (PL) spectroscopy were utilized. A detailed discussion of these results is presented in the following sections.

2.4 XRD analysis

The structural properties were confirmed by PXRD (Fig. 1.9). PXRD pattern of aggregated CDs powder suggests the peak at 25° corresponding to (002) plane present in both ODA and GDA confirms the graphitic carbon core formatio,n and 41° corresponding to (100).[25]

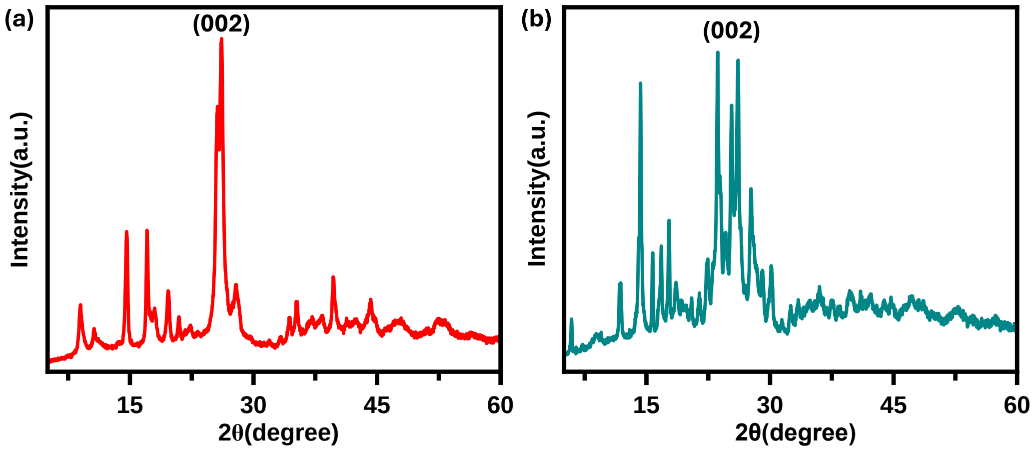

Fig. 1.9 The PXRD analysis of ODA and GDA aggregates.

2.5 FESEM analysis

To analyse the morphology of aggregated CDs, the ODA and GDA samples were subjected to Field Scanning Electron Microscopy (FESEM) demonstrated in Fig. 2.1 The FESEM revealed uniform spherical aggregated structures of average size 0.89 mm and 0.68 mm, for ODA and GDA, respectively. Interestingly, these spherical aggregated structures are interconnected to each other through a stick-like structure. The adaptation of the spherical shape of CDs during aggregation is perhaps because of the minimization of contact with water or the hydrophobic effect of molecular assembly involved in CDs.

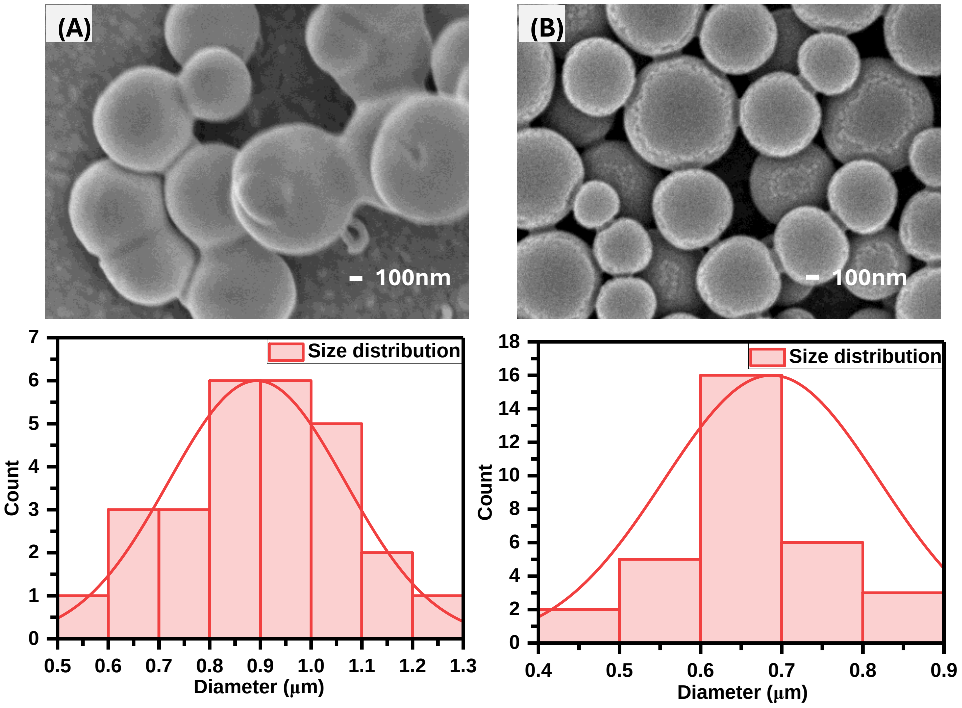

Fig. 2.1 (a) ODA thin film analysis and corresponding particle size distribution in material and (b) GDA with corresponding particle size distribution in sample.

The hydrophobic nature of CDs can be attributed to the surface functional group originating from the selection of precursors used during synthesis. Additionally, the compact structure and lack of polar surface groups can further enhance hydrophobicity. However, the morphology of OD and GD could not be captured due to presence of acetic acid and their hygroscopic nature as well as FESEM instrument compatibility to solid state samples.

2.6 Contact angle measurement

The contact angle found to be 137.7° for ODA mixed with the binder polyvinylidene fluoride (PVDF) and coated over mild steel. On the other hand, GDA showed a compromised contact angle of 117.8° under similar experimental conditions to ODA (Fig. 2.2). The significant difference in contact angle of ODA and GDA may be due to the availability of hydrophobic atoms over the surface of aggregated CDs.[26]

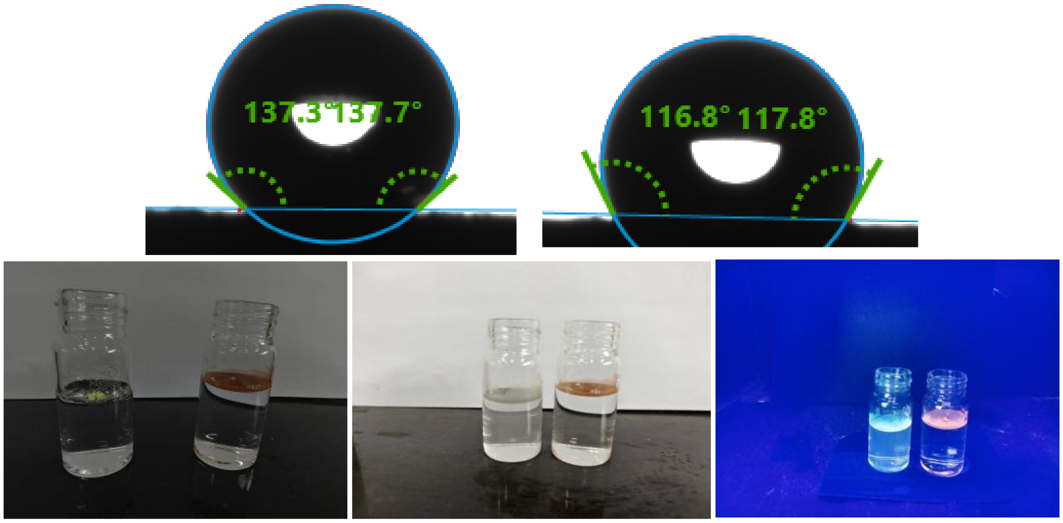

Fig. 2.2 Demonstration of hydrophobicity and the contact angle measurement.

2.7 Functional group analysis

The FT-IR spectra of aggregated carbon dots (CDs) were recorded to identify the surface functional groups and chemical bonds present (Fig. 2.3) in ODA and GDA. A prominent peak at 1676 cm-¹, 1666 cm-¹ for ODA and GDA, respectively, is attributed to the C=O stretching vibration of amide groups, confirming the successful amidation of the precursor materials. Peaks at 1586, 1560, 1460, and 1416 cm^{-1} for ODA and 1586, 1535, 1492, and 1394 cm-1 for GDA are associated with the symmetric and antisymmetric stretching vibrations of aromatic ring structures, indicating the aromatic framework remains intact during carbonization.[23] Additional peaks at 1259, ~1034, and 695 cm^{-1} are assigned to the stretching vibrations of C–N, C–O, and C–S bonds, respectively. Notably, the peak present in both the ODA and GDA at 550 cm-1 confirms the presence of the S–S bond. The S-S bond is also well known for playing a critical role in imparting stable fluorescence properties to the CDs.

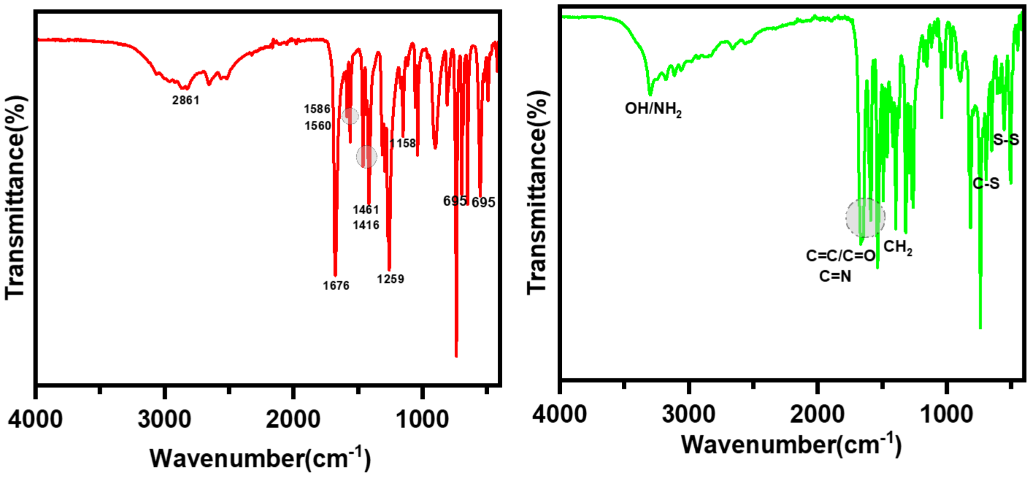

Fig. 2.3 Functional group analysis by FTIR spectroscopy for ODA and GDA aggregation.

2.8 UV-Visible analysis

To explore the optical properties of ODA and GDA, detailed UV-visible and fluorescence experiments were performed as demonstrated in Fig 4. The solid-state UV-vis of ODA displayed a broader absorption spectrum extending from the UV to the visible region, with a prominent peak around

345 nm may be attributed to π-π* transitions of C=C and shoulder around 450 nm suggesting n-π* transitions of C-N/S and another smaller shoulder at 557 nm due to n-π* of C=O and C=O/S. Further, freshly prepared solid-state ODA was subjected to the fluorescence spectrophotometer which showed the excitation peak at 557 nm. Furthermore, it demonstrated the emission peak centred at 600 nm upon excitation at 557 nm (Fig. 2.4). On the other hand, solid state GDA showed a broader absorption peak around 250 nm which may be assigned to π-π* electronic transitions of C=C and a weaker shoulder at longer wavelengths 450 nm indicates the n-π* transitions of C=O or C-N/S. Further, the excitation profile obtained from the fluorescence spectrophotometer also confirms suitable excitation at 450 nm. Considering 450 nm as excitation value, an emission peak found to be at 500 nm. Further, the Stokes shift was calculated to be 43 and 50 nm corresponding to the ODA and GDA, respectively.[27]

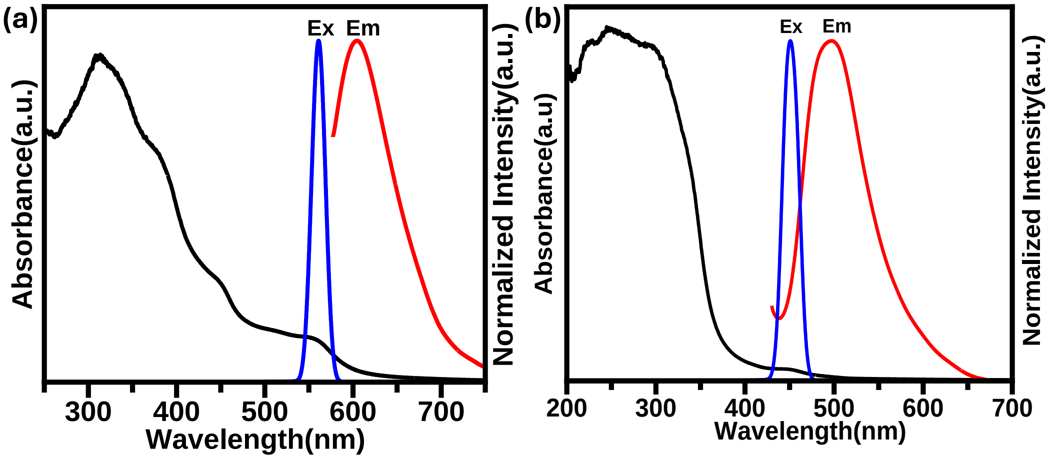

Fig. 2.4 (a) and (b) UV-visible absorbance spectroscopy for ODA and GDA aggregates with corresponding emission and excitation behaviour.

2.9 Fluorescence titration experiment

GDA are aggregated CDs, a fluorescence titration studies between the CDs and water performed. The original acetic acid mediated OD or GD showed emission at 605 (λ_{ex} 560 nm) and 500 nm (λ_{ex} 450 nm), respectively. The excitation-independent experiments also support the emission at 605 and 500 nm for OD and GD, respectively (Fig. 6). Further, upon aliquot addition of water produced red-shifted peaks at 600 and 500 nm at the expense of diminishing the original peaks corresponding to OD and GD suggests the aggregation-induced emission caused colour change in **ODA** and **GDA**.[10] The emission at 600, 500 nm for ODA and GDA supports their solid-state orange and green colour fluorescence, respectively (Fig. 2.5).

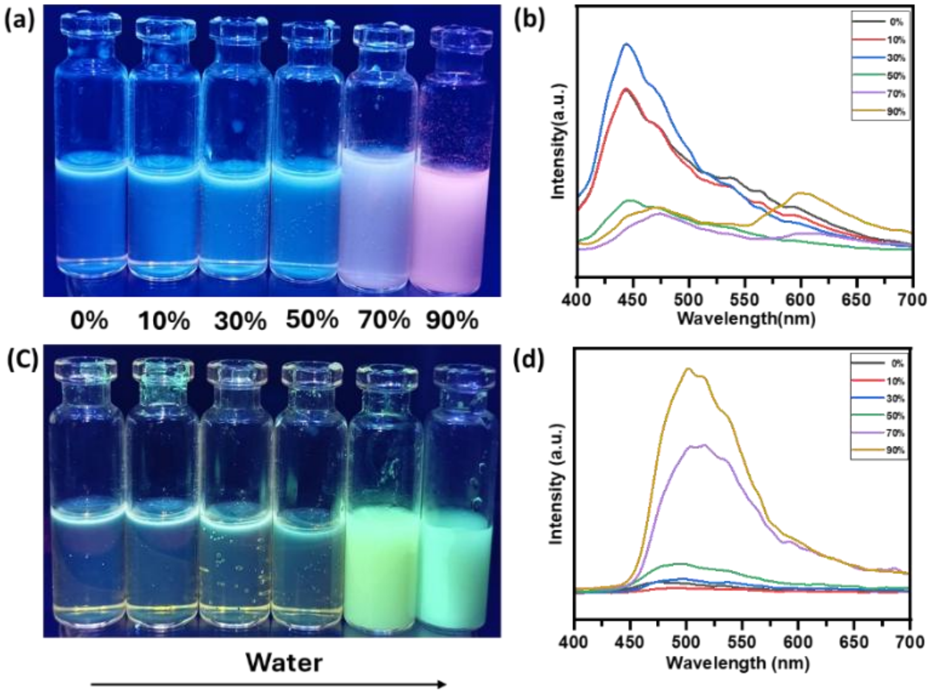

Fig. 2.5 Fluorescence titration experiment under 365nm excitation wavelength for ODA and GDA experiment.

2.9.1 Photoluminescence

To further validate the distinct emission characteristics observed from ODA and GDA composites, their respective chromaticity coordinates were examined using Commission Internationale de l'Éclairage (CIE) diagrams, derived from the same set of photoluminescence data previously discussed. As illustrated in **Fig. 2.6**, the CIE coordinate for the ODA-based material was determined to be **(0.54, 0.45)**, placing it firmly within the orange region of the chromaticity diagram. This quantitatively supports the visually observed orange fluorescence emitted from the ODA composite under UV excitation. In contrast, the CIE coordinate for the GDA sample was measured at **(0.22, 0.35)**, a location within the blue-green region of the diagram. The difference in emission colours between the two samples is not only visually distinct but is also captured precisely through this shift in chromaticity coordinates.

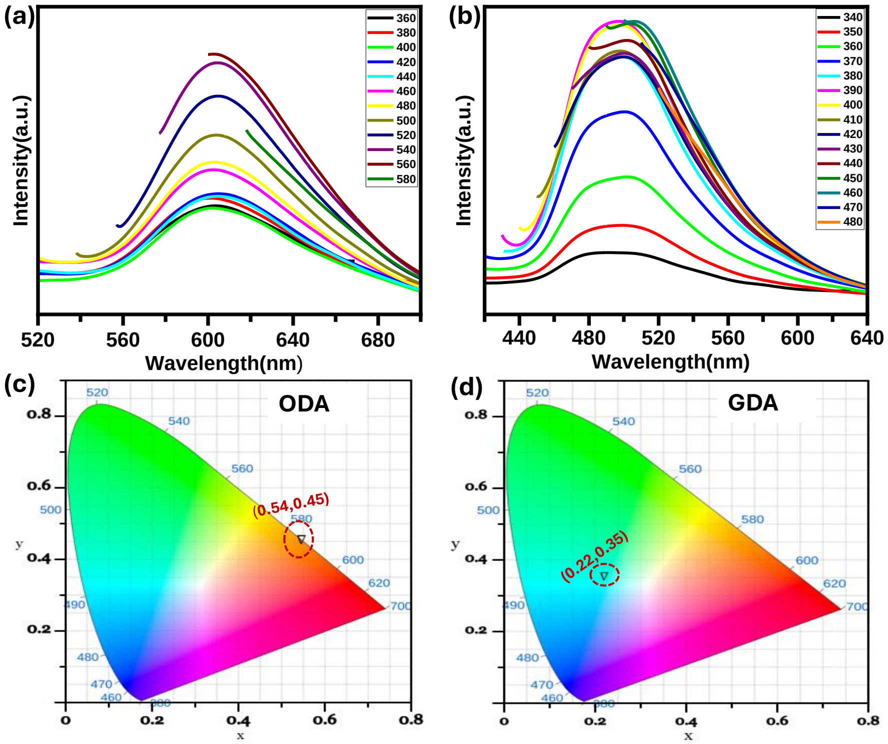

Fig. 2.6 (a-b) represents the excitation independent behavior of ODA and GDA further more (c-d) CIE coordinates confirms the orange and green fluorescence of ODA and GDA aggregates.

This variation in CIE values highlights the tunable optical behavior of the synthesized carbon dot materials. These findings hold promising implications for a range of colour-specific optoelectronic applications. For instance, precise control of emission colour is vital in the development of advanced light-emitting diodes (LEDs), where colour purity and stability are critical. Similarly, in the emerging field of fluorescence tunable lenses (FTLs), the ability to shift emission based on material design opens new avenues for adaptive optics and smart display technologies. Overall, the CIE chromaticity analysis not only substantiates the visual observations of emission colour but also underscores the strategic advantage of carbon dot systems in enabling customizable and functional photonic devices. [28]

Applications

LEDs fabrication and testing

Specifically, organic-derived aggregates (ODA) and green-emitting dot aggregates (GDA) were explored for their ability to act as fluorescent materials when integrated into an epoxy resin matrix. This approach not only leverages the unique optical characteristics of CDs but also allows facile integration with commercially available UV LED systems. To prepare the composite, powdered forms of ODA and GDA were homogeneously mixed with a transparent epoxy resin. This mixture was then cast into a mould over the UV LED chip, creating a conformal and protective fluorescent layer directly above the light source, as shown schematically in **Fig. 2.7**. The curing process was allowed to proceed at room temperature for approximately one hour to ensure proper hardening and uniform dispersion of the emissive material throughout the polymer matrix. Once cured, the LEDs, equipped with the fluorescent composite layers, were powered using a standard 3.2 V direct current supply. The UV LED chips used in this study emitted at a wavelength of 365 nm, which served as the excitation source for the photoluminescent CDs. Upon excitation, distinct emissions were observed depending on the CD composite used. The ODA-based polymer composite exhibited a strong orange fluorescence, whereas the GDA-based composite produced a vivid green emission. These emission colours were not only This method offers a scalable and cost-effective pathway for developing customized LED lighting solutions, where emission colour can be tailored by simply varying the type of CDs used. Moreover, the compatibility of CDs with polymer matrices like epoxy resin ensures robustness and long-term operational stability. As such, this work presents a meaningful step forward in the design of luminescent devices for applications ranging from decorative lighting to optoelectronic displays

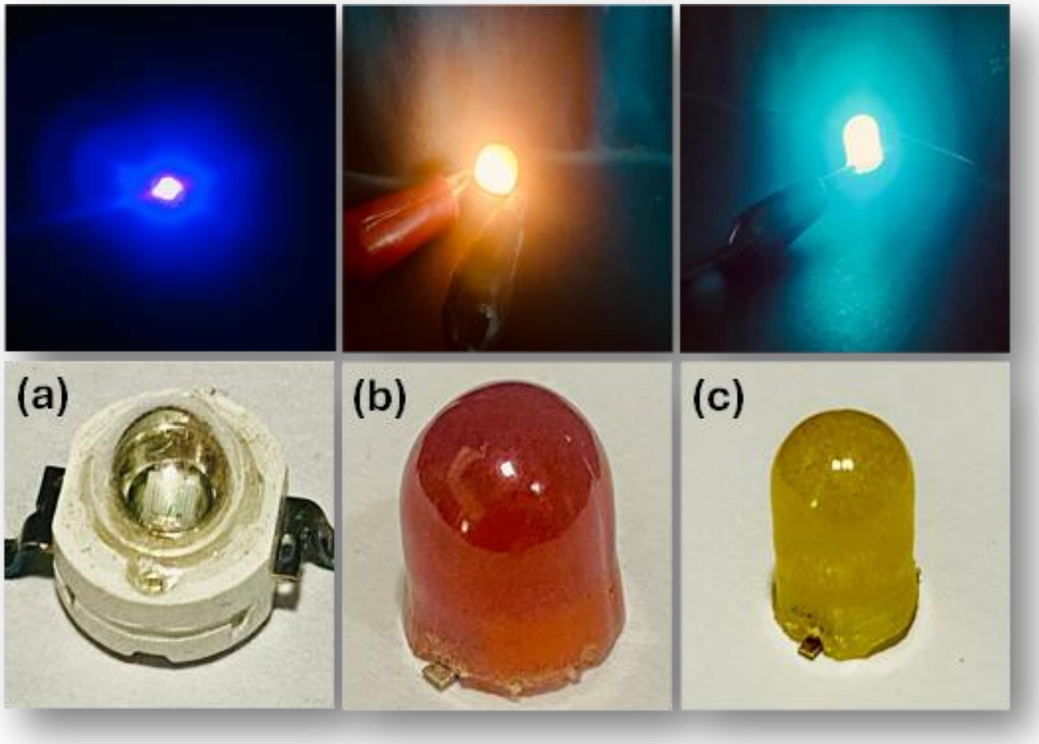

Fig. 2.7 demonstration of fabricated LEDs from ODA and GDA aggregates under 3.2V .

Fingerprint detection

Owing to the versatile characteristics of carbon dots (CDs), their use for latent fingerprint detection is a viable and novel research avenue. For a common experimental process, an unsoiled glass slide was initially employed as the substrate for recording a latent fingerprint. A natural thumbprint was applied by softly pressing the thumb against the glass surface, which left behind non-visible residues made up of sweat, oils, and other trace biomaterials. Then, fluorescent CD aggregates, in the form of a powder, were evenly sprayed across the slide. The fluorescent particles attached preferentially to the tiny secretions on the skin remaining in the fingerprint and permitted high-contrast visualization. When illuminated by suitable excitation light—

preferably in the UV region—the treated fingerprint fluoresced, displaying complex patterns of ridges. As seen in Fig. 2.8, all of the major minutiae of the fingerprint were clearly seen, including ridge endings, bifurcations, islands, enclosures, deltas, and the core. These are the most important features to consider for biometric examination and forensic identification. The capacity of CDs to light up these delicate structures shows their promise as a sensitive, non-destructive, and affordable instrument in forensic science. This strategy not only enhances the realistic usefulness of CDs in situ but also provides additional avenues for improving their composition and fluorescence characteristics for better contrast, specificity, and environmental stability in forensic use.

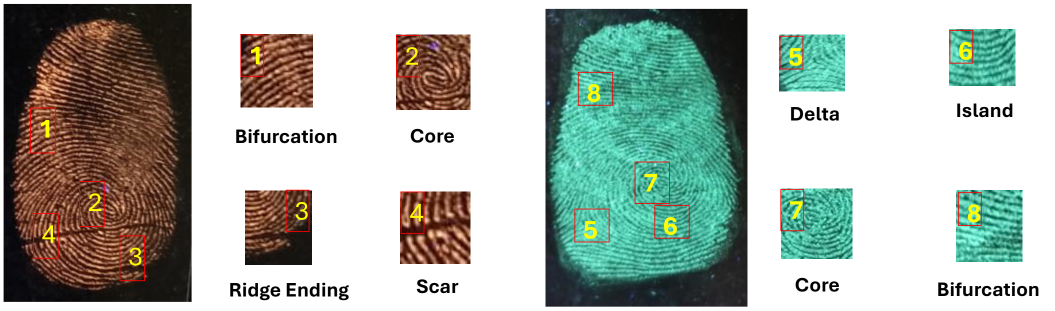

Fig. 2.8 ODA and GDA applications in fingerprint detection all the subparts: bifurcation, core, ridge ending scar of thumbprint are neat and clear.

Chapter 3

Metal-doped carbon dot aggregates and their applications

Overview

Researchers have prepared red-emitting, hydrophobic carbon nanodots with solid-state fluorescence and aggregation-induced emission (AIE) character. They did so using 2,2'-dithiodibenzoic acid as the source of carbon and manganese acetate as the dopant in a water-ethanol solvent mixture. The resulting CDs have a distinct structure around disulfide bridges, which allows rotational freedom when dispersed but inhibits motion upon aggregation, initiating the AIE effect. To further understand the formation mechanism, comparative experiments were conducted emphasizing changes in the carbon source, dopant source, and solvent composition. These CDs showed potential practical applications in color-tenable anticounterfeiting technologies and monochromatic emitters for LED devices.

In this work, Ni-doped CDs and their aggregates were successfully synthesized by a step solvothermal method with the same set of conditions without doping. These synthesized CDs aggregates, called M-CDs and W-CDs. The detailed study has been discussed in the various characterization techniques like XRD, FESEM, Contact angle, UV-visible spectroscopy, etc.

3.1 Synthesis of metal-doped carbon dot aggregates

The solvothermal method was used for the synthesis of CD aggregates. In synthesis, I replaced one precursor, adenine or p-aminobenzenethiol, with a metal precursor.

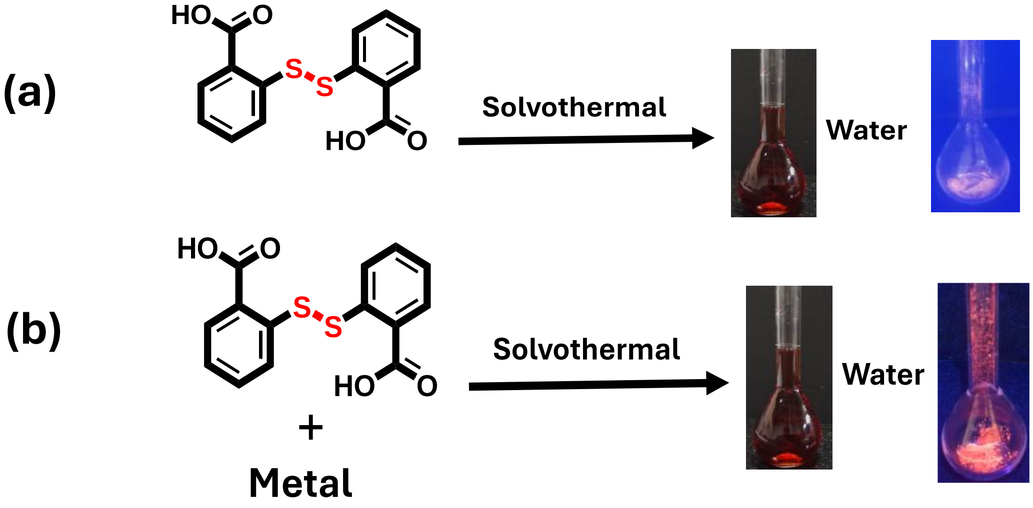

Fig. 2.9 The typical synthesis process demonstration of W-CDs and M-CDs.

Result and discussion

3.2 Structural and morphological study

The structural and morphological study in the part did a comparative tow combinations synthesized by a step solvothermal method, one is M-CD (metal-doped carbon dots) and the other is W-CD (without metal carbon dots). The peak around 25° in both confirms that the graphitized carbon core has formed in the carbon dots. The decrease in intensity in Fig. c might be due to the metal precursor in the XRD plot and FESEM analysis shows the aggregated flower-like structure. And another thing absorbed from this morphology of M-CDs aggregates, the metal precursors do not affect morphological properties only optical properties tune in a usual way to use in the optoelectronic applications.

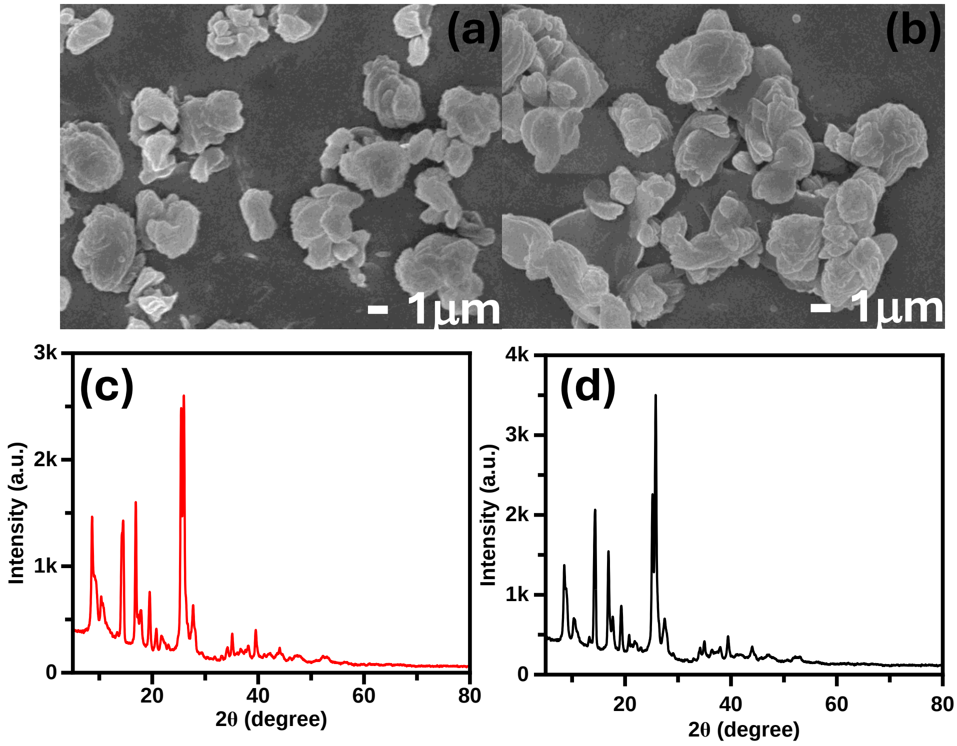

Fig. 3.1 (a-b) FESEM images and (c-d) XRD plots for M-CD and W-CDs, respectively.

3.3 Study of optical properties

In the order of study, both M-CD and W-CD are characterized by UV-visible spectroscopy and photoluminescence spectroscopy. Fig (a-b) absorbance spectra clearly show a drastic increase in the M-CD. The metal precursors are responsible for this change. The broad peak around 260-390nm shows π-π^* transition, but the peak 555nm is due to n-π^* transition. Now, to determine the fluorescence properties, a fluorescence experiment was performed, and w-CD shows very little fluorescence in the orange(600nm) region after adding the metal precursor; this fluorescence has been shifted to the red (628nm) region so another effect we can absorb due to metal dopping. This addition of metal precursor make the suitable for optical properties of synthesized M-CD aggregates.

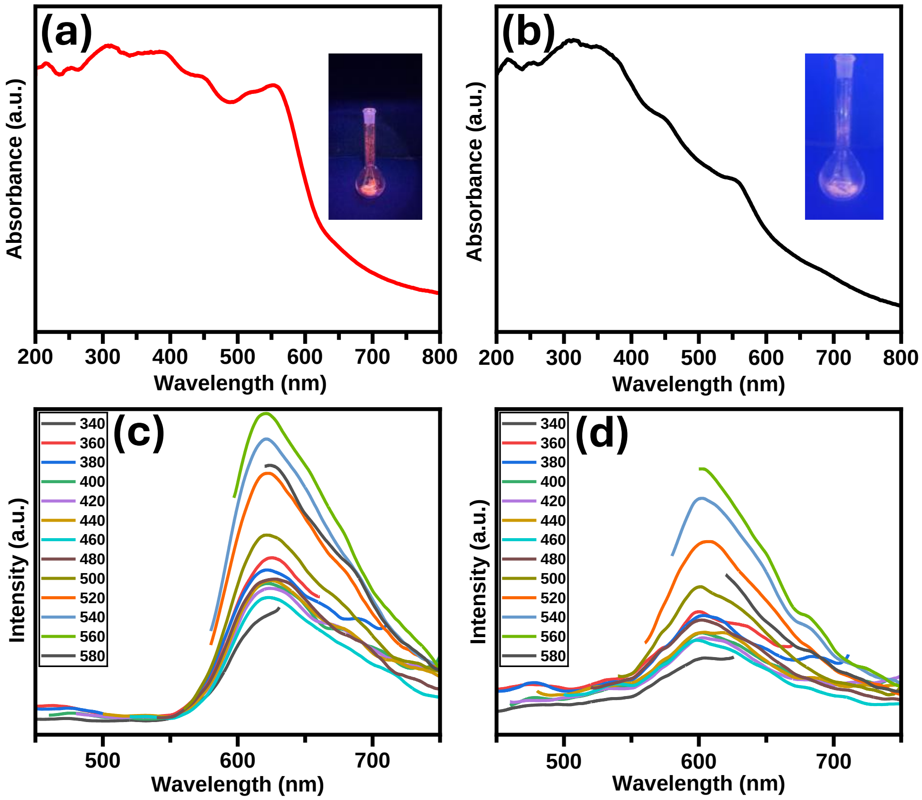

Fig. 3.2 (a-b) absorbance spectra and (c-d) the photoluminescence plot for M-CDs and W-CDs, respectively.

3.4 Applications of synthesized CD aggregates

The synthesized carbon dots have shown excellent potential for practical applications, particularly in fingerprint detection and as a security ink. For fingerprint detection, I first pressed my thumb onto a glass slide and then sprayed the carbon dot powder onto it. Under UV light, the thumbprint became clearly visible, revealing fine details. To achieve white light emission, these carbon dots were embedded in a PVA polymer matrix. In the fabrication of LEDs, the aggregated M-CDs were mixed with epoxy resin and coated onto a UV-LED. This process successfully converted the UV light into visible light.

For security ink applications, the aggregated carbon dots were dissolved in methanol and directly applied to filter paper. Under UV light, the ink displayed strong fluorescence, making it ideal for security and anti-counterfeiting uses. These versatile applications, ranging from fingerprint detection to security inks and light-emitting devices, highlight the significant role of these carbon dots in everyday life and underscore their value in the field of materials science.

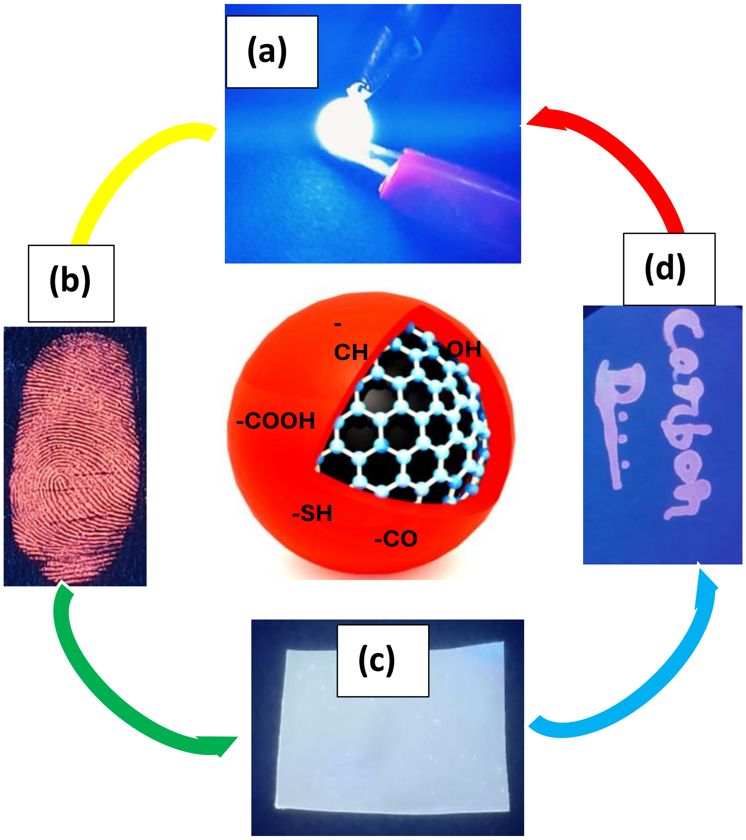

Fig. 3.3 (a, b, c, and d) are LED, fingerprint detection, polymer composite, and security purpose ink, respectively, the applications of the M-CDs.

Chapter 4

Conclusion of synthesized CD aggregates

Conclusions

CDs possessing short-wave emission luminescence in an aqueous state and long-wave emission in a solid state were successfully synthesized via a facial method. Further, our experiments proved that the disulfide bond played a major role in AIE. Meanwhile, intramolecular disulfide bond rotation is prohibited, and the energy conversion at the surface is converted into long-wave emission fluorescence. First, CD aggregates ODA and GDA were synthesized and applied to LED applications. Due to the high contrast of ODA and GDA, we have used them in fingerprint detection. It may be helpful for a forensic laboratory.

Furthermore, another metal-doped carbon dot aggregate synthesis has been done with high contrast red fluorescence. These M-CD aggregates are used in LEDs, fingerprint detection, as well as in polymer composites and security purpose inks. So, synthesized ODA, GDA, and M-CDs aggregates could be used in multipurpose (LEDs, Fingerprint detection, polymer composites, security purpose inks) applications.

Future scope

Due to their hydrophobic nature, carbon dots (CDs) hold great potential for various future applications. In corrosion protection, their ability to repel water can help prevent the penetration of moisture and corrosive agents to metal surfaces, thus improving durability. For fingerprint detection, CDs can be used to enhance image clarity due to their fluorescence and compatibility with different surfaces. Their water-repellent properties also make them suitable for developing hydrophobic coatings, useful in self-cleaning and anti-fogging surfaces.

When incorporated into polymers, CDs can contribute to the formation of flexible and functional materials with added optical or mechanical properties. Additionally, the strong photoluminescence and stability of CDs make them promising materials for LED fabrication, especially in the development of cost-effective and environmentally friendly light-emitting devices. These features suggest a wide scope for carbon dots in future scientific and industrial applications.

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Colour-tuneable hydrophobic carbon dot aggregates for LEDs applications†

Dharmendra Kumar,[a] Bharat Kumar Sahu,[a] Abul Kalam[b] and Mrigendra Dubey *[a]

Solid-state fluorescent carbon dot (CD) aggregates were synthesized by the reaction of 2,2′-dithiosalicylic acid with adenine/4-amino benzene thiol using solvothermal and precipitation methods. Blue-emissive OD and GD CDs were transformed into the orange- and green-emissive solid-state CD aggregates ODA and GDA upon treatment with water, respectively. This water-triggered aggregation-induced emission was responsible for the switching of the emission from blue to orange/green. Interestingly, ODA and GDA revealed reversible emission upon solid–liquid–solid switching. Contact-angle measurements suggested the hydrophobic nature of ODA and GDA. ODA and GDA were utilized to fabricate a fluorescent polymeric cover of a light-emitting diode.

Carbon dots (CDs) are zero-dimensional eco-friendly nanoparticles. They have garnered interest due to their versatile properties such as fluorescence, nontoxicity, and biocompatibility. CDs have significant applications in various fields such as anticounterfeiting, optoelectronics, energy storage, supercapacitors, batteries, solar energy conversion, and solar cells.[1–4] Although most CDs have been reported to be highly soluble in water and typically found in liquid form, they often encounter significant challenges during drying and can undergo aggregation-caused quenching (ACQ).[5] In other words, during solidification CDs tend to establish interactions, leading to excessive fluorescence resonance energy transfer and a marked reduction in fluorescence intensity. To overcome ACQ, CDs are incorporated into a polymeric matrix to retain the original fluorescence for a long time, but polymers affect the applicability of CDs.[6,7] Due to these challenges, solid-state CDs have been less explored and utilized compared with liquid-state CDs. However, several research teams have tried to solve ACQ-related problems by varying the substrates, solvents as well as solvothermal reaction conditions. However, it remains challenging to retain the fluorescence properties of CDs in the solid state. Furthermore, using a supramolecular engineering approach, CDs can be triggered to undergo aggregation under the influence of water to achieve aggregation-induced emission (AIE) in the solid state.[8,9]

CDs represent a promising class of nanomaterials for the forthcoming generation of lighting and display technologies, which is attributable to their tunable band gap, high quantum yield, and remarkable stability. To achieve the desired fluorescence colour with high emission intensity in solid-state CDs, researchers have explored various strategies, including regulation of size, shape and morphology, surface functionalization, and heteroatom doping (particularly N and S atoms) to attain suitable excited energy levels.

Among fourth-generation lighting technology, light-emitting diodes (LEDs) have emerged as promising energy-saving, durable as well as efficient luminous sources. In addition to CDs, europium-based materials have also been effectively used for white light-emitting diode (WLED) fabrication due to their excellent luminescent properties.[10–12] However, such rare earth metal-based materials are often costly, making them less suitable for large-scale sustainable applications. In recent years, CDs have been employed as smart materials for the fabrication of high-color-purity LEDs following photoluminescence and electroluminescence mechanisms.[13] The cost-effectiveness, development and utilization of photoluminescence are better than electroluminescence. To follow the photoluminescence mechanism, multicoloured emissive CDs-polymer composites have been used as phosphor-coating materials on ultraviolet chips or on blue chips. However, the design of desired fluorescent CDs followed by incorporation into a polymer matrix to achieve a transparent CDs-polymer composite material for the fabrication of high-color-purity LEDs remains a challenge.

Taking into account the aforementioned challenges to synthesize ACQ-free, AIE-efficient, fluorescent solid-state CDs for LED coating applications, we chose 2,2′-dithiosalicylic acid

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[a] *Soft Materials Research Laboratory, Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Indore, Indore-453552, India. E-mail: mdubey@iiti.ac.in*

[b] *Department of Chemistry, College of Science, King Khalid University, Abha 61413, Saudi Arabia*

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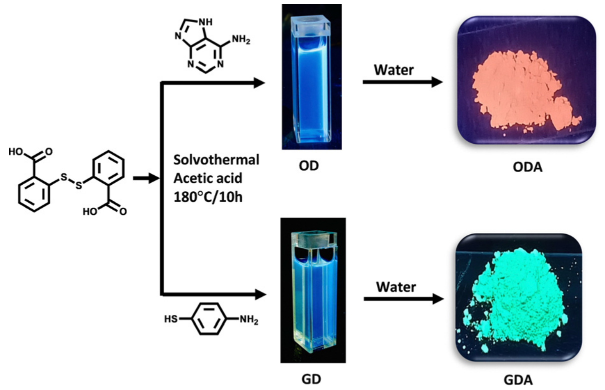

Scheme 1 Synthesis of the carbon dots aggregates **ODA** and **GDA** (schematic).

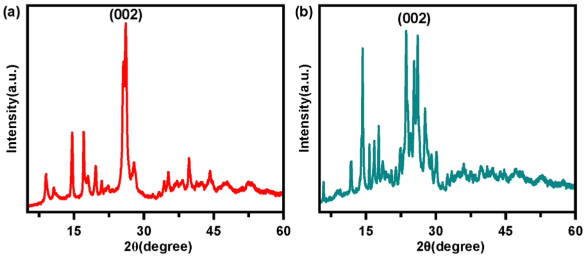

Fig. 1 Powder X-ray diffraction pattern of aggregated (a) **ODA** and (b) **GDA**.

(DTSA) as the carbon and sulfur source, and adenine/4-aminobenzenethiol served as nitrogen sources (Scheme 1). The presence of a disulfide bond (S–S) may hinder π–π stacking and, in turn, overcome the problem of ACQ in solid-state CDs. In addition, the nitrogen-rich adenine and *p*-amino benzenethiol may contribute to the regulation of the emission properties, offering a method to synthesize fluorescent CDs. It is also expected that functionalized CDs will undergo further aggregation under the influence of water but also impart fluorescence through AIE in the solid state. The carbon dot **OD** was synthesized by a solvothermal reaction between DTSA and adenine in acetic acid (Experimental section, ESI†). Furthermore, the obtained **CD** solution was purified by centrifugation followed by the separation of large particles using a syringe filter.

The blue-emissive pure **CD** solution was further treated with hot DI water and, in turn, CDs precipitated out from the solution. This water-assisted precipitation was helpful in obtaining pure solid-state CDs but also triggered AIE to produce solid-state ODA-CDs (Scheme 1). In other words, the blue-emissive **OD** solution was transformed into orange-emissive solid-state **ODA** under the influence of water. Interestingly, the substitution of adenine with 4-aminobenzenethiol produced the green-emissive aggregated solid-state CDs **GDA** under similar reaction conditions to **ODA**, which signified the importance of heteroatoms to tune the emission properties in CDs. Notably, the dissolution of **ODA** and **GDA** into methanol produced a blue-emissive solution but, upon drying, it turned orange and green, respectively. In other words, **ODA** and **GDA** having reversible emission upon solid–liquid–solid switching may have been due to aggregation–segregation–aggregation, respectively. **ODA** and **GDA** were characterized by FTIR spectroscopy, FESEM, XRD, and spectrophotometry. The structural properties of **ODA** and **GDA** were confirmed by powder X-ray diffraction (PXRD) within a scanning range of 3–80° (Fig. 1). The PXRD pattern of aggregated CDs powder revealed peaks at 25° and 41° corresponding to the (002) and (100) planes in both **ODA** and **GDA**, thereby confirming the formation of a graphitic carbon core in CDs.[9]

To analyse the morphology of aggregated CDs, the **ODA** and **GDA** samples were subjected to field emission scanning electron microscopy (FESEM) (Experimental section, ESI†). FESEM revealed uniform spherical aggregated structures of average size 0.89 μm and 0.68 μm for **ODA** and **GDA**, respectively (Fig. 2 and Fig. S1, S2, ESI†). Interestingly, these spherical aggregated structures were interconnected to each other through a stick-like structure. Adaptation of the spherical shape of CDs during aggregation was perhaps because of the minimization of contact with water or the hydrophobic effect of the molecular assembly involved in CDs. The hydrophobic nature of CDs can be attributed to the surface functional group originating from the selection of precursors used during synthesis. The contact angle was found to be 137.7° for **ODA** mixed with the binder polyvinylidene fluoride (PVDF) and coated over mild steel. Conversely, **GDA** showed a compromised contact angle of 117.8° under similar experimental conditions to **ODA** (Fig. S4 and S5, ESI†).[14] The significant difference in the contact angle of **ODA** and **GDA** may have been due to the availability of hydrophobic atoms over the surface of aggregated CDs.[15] Additionally, the compact structure and lack of polar surface groups can further enhance hydrophobicity. However, the morphology of **OD** and **GD** could not be captured due to presence of acetic acid and their hygroscopic nature, as well as the compatibility of the FESEM instrument to solid-state samples.

The FT-IR spectra of aggregated CDs were recorded to identify the surface functional groups and chemical bonds

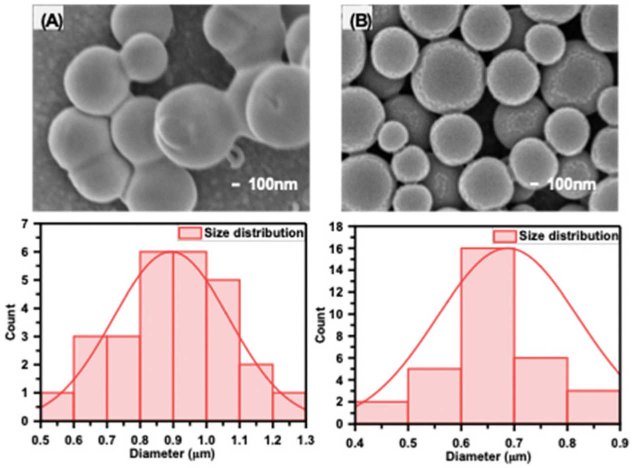

Fig. 2 FESEM images of (A) **ODA** and (B) **GDA** along with their average particle size histogram.

present in **ODA** and **GDA** (Fig. S3, ESI†). A prominent peak at 1676 cm^{-1} and 1666 cm^{-1} for **ODA** and **GDA**, respectively, was attributed to the C=O stretching vibration of amide groups, confirming the amidation of precursor materials. Peaks at 1586, 1560, 1460, and 1416 cm^{-1} for **ODA** and 1586, 1535, 1492, and 1394 cm^{-1} for **GDA** were associated with the symmetric and antisymmetric stretching vibrations of aromatic ring structures, indicating that the aromatic framework remained intact during carbonization.[6,16] Additional peaks at 1259, ~1034, and 695 cm^{-1} were assigned to the stretching vibrations of C–N, C–O, and C–S bonds, respectively. Notably, the peak present in **ODA** and **GDA** at 550 cm^{-1} confirmed the presence of the S–S bond. The S–S bond is well known for playing a critical part in imparting stable fluorescence properties to CDs (Fig. S3, ESI†).

To explore the optical properties of **ODA** and **GDA**, detailed UV-visible spectroscopy and fluorescence experiments were performed, as demonstrated in Fig. 3. The solid-state UV-vis spectra of **ODA** displayed a broader absorption spectrum extending from the UV to the visible region, with a prominent peak around 345 nm (attributed to π–π* transitions of C=C), a shoulder around 450 nm (suggesting n–π* transitions of C–N/S) and another smaller shoulder at 557 nm (due to n–π* of C=O and C=O/S). Furthermore, freshly prepared solid-state **ODA** was subjected to fluorescence spectrophotometry. **ODA** showed an excitation peak at 557 nm, and an emission peak centred at 600 nm upon excitation at 557 nm (Fig. 3).[17]

In contrast, solid-state **GDA** showed a broader absorption peak around 250 nm (which could be assigned to the π–π* electronic transitions of C=C) and a weaker shoulder at 450 nm (indicating the n–π* transitions of C=O or C–N/S). Furthermore, the excitation profile obtained from fluorescence spectrophotometry confirmed suitable excitation at 450 nm. Considering 450 nm as the excitation value, an emission peak was found at 500 nm. The Stokes shift was calculated to be 43 and 50 nm corresponding to **ODA** and **GDA**, respectively.[9,18] The narrow excitation profile compared with emission for **ODA** and **GDA** was a consequence of the Franck–Condon principle.[19]

To confirm **ODA** and **GDA** were aggregated CDs, fluorescence titration studies between CDs (OD/GD) and water were performed (Fig. 5). The original acetic acid-mediated **OD** or **GD** showed emission at 445 nm and 473 nm (at fixed excitation (λ_{ex}) of 365 nm), respectively. Interestingly, upon aliquot addition of 70% water, a new peak appeared at 605 and 500 nm for **OD** and **GD**, respectively. Remarkably, the spectral change observed was found to be consistent with the visual results obtained under UV light (λ_{ex} = 365 nm) and by the naked eye (Fig. 5). The blue-emissive **OD** solution turned orange-pink upon maintaining 90% water content, indicating the formation of aggregated **ODA**. Conversely, **GD** turned into a blue–green turbid solution of **GDA** at addition of 90% water. The excitation-independent experiments also supported the emission at 605 and 500 nm for **ODA** and **GDA**, respectively (Fig. 4). The excitation-independent behaviour of **ODA** and **GDA** suggested fewer surface defects and uniform size distribution.[20] In other words, aliquot addition of water (90%) produced red-shifted peaks at 605 and 500 nm at the expense of diminishing the original peaks corresponding to **OD** and **GD**, suggesting that aggregation-induced emission caused colour changes in **ODA** and **GDA.**[21,22]

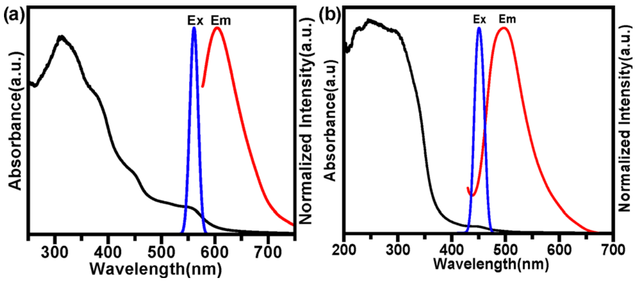

Fig. 3 UV-vis absorbance with the excitation–emission plot of (a) **ODA** and (b) **GDA**.

The emission at 600, 500 nm for **ODA** and **GDA** supported their solid-state orange and green fluorescence, respectively (Fig. 4). In order to support the aforementioned observation about emission color, the CIE coordinates were acquired for **ODA** and **GDA** using the same set of data as demonstrated in Fig. 4. The emission point with CIE coordinates found to be at (0.54, 0.45) lay in the orange region, showcasing orange fluorescence for **ODA**, while the emission point labelled at (0.22, 0.35) fell in the region of blue-green emission, indicating a material emitting light in the blue green, but predominantly towards the green, spectrum.[23] The inclusion of two-colour emission might have been the reason behind the broader spectrum of **GDA** compared with **ODA.**

The shift in chromaticity coordinates between the two figures highlighted the tuneable optical properties of the materials, potentially influenced by variations in synthetic conditions or chemical modifications. These findings are significant for applications in colour-specific technologies such as LEDs and fluorescence-tuneable lenses.

To fabricate high-colour-purity UV LEDs following photoluminescence mechanisms, **ODA** or **GDA** powders wee mixed with

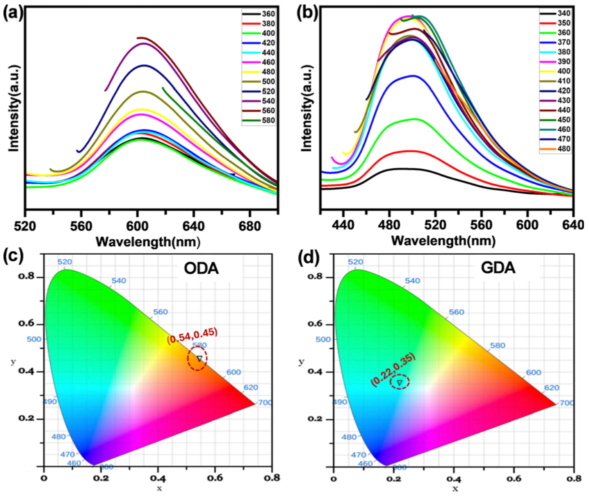

Fig. 4 Photoluminescence spectra at different excitation wavelengths along with CIE coordinates of (a) and (c) **ODA** and (b) and (d) **GDA** CDs powder.

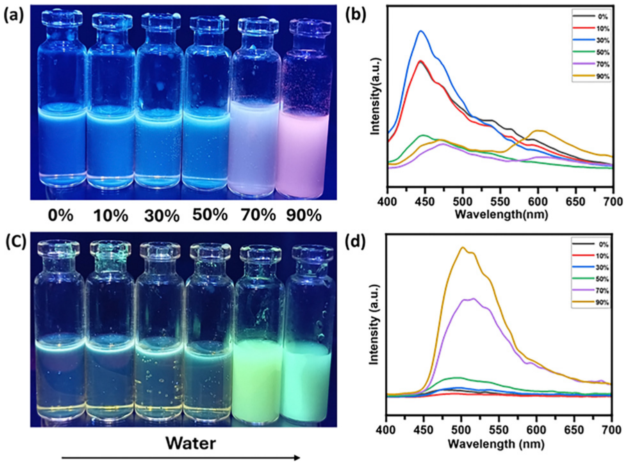

Fig. 5 (a) and (c) Demonstration of water-triggered aggregation-induced emission of an acetic acid **OD** and **GD** CDs solution and formation of **ODA** and **GDA** under UV light (λ_{ex} = 365 nm). (b) and (d) Aliquot addition of water to **OD** and **GD** solutions (λ_{ex} = 550, **OD** and 450 nm, **GD**).

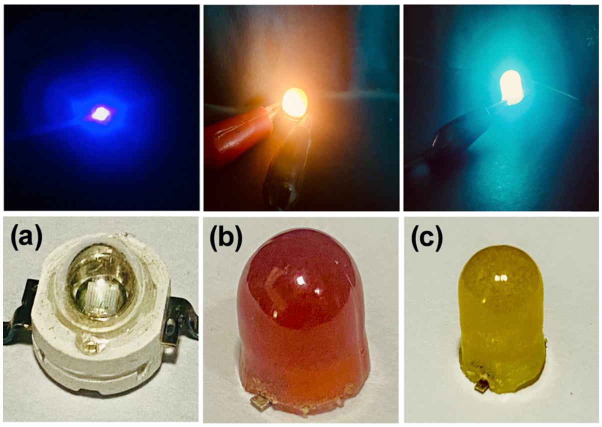

Fig. 6 LED fabrication and illumination at 3.2 V (a) without CDs, (b) with an **ODA** cover and (c) a **GDA** cover.

epoxy resin to acquire a mould over a UV LED, as demonstrated in Fig. 6 (Experimental section, ESI†). After 1 h of setting time, LEDs of 365 nm were illuminated by a power supply at 3.2 V. The **ODA**-polymer composite produced orange LEDs, while the **GDA**-based composite emitted a green colour. The glowing fluorescence satisfied the aforementioned CIE coordinates.

Conclusions

The aggregated solid-state CDs **ODA** and **GDA** were synthesized using solvothermal and precipitation methods. These aggregate powders were characterized using FT-IR spectroscopy, UV-vis spectroscopy, fluorescence studies, PXRD and FESEM. The presence of AIE was established by fluorescence titration followed by FESEM. **ODA** was more hydrophobic in nature than **GDA** according to contact-angle measurements. Furthermore, owing to excellent fluorescence properties and photostability, we fabricated multicolour LEDs by applying **ODA** and **GDA** CDs aggregates. The fabricated LEDs possessed decent device performances by following a photoluminescence mechanism. Various types of colour-tuneable LEDs could be fabricated by following this simple and cost-effective approach.

Author contributions

MD: methodology, project administration, resources, conceptualization, funding acquisition, supervision, visualization, and writing (original draft). DK: data curation, methodology, validation, visualization, and figure creation. BKS: Helped DK in instrumentation, data analysis, and figure creation AK: visualization, discussion, review and editing.

Data availability

All the original experimental data for this study (FT-IR spectroscopy, UV-vis spectroscopy, fluorescence studies, contact-angle measurement and FESEM) have been provided in the main text, and ESI† is available upon reasonable request *via* email.

Conflicts of interest

There are no conflicts of interest to declare.

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