Production of carbon nanodots from hydrothermal carbonisation of durian shell waste

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**PRODUCTION OF CARBON NANODOTS FROM HYDROTHERMAL
CARBONISATION OF DURIAN SHELL WASTE**

J.R.A. SUPULI JAYAWEERA

**INTERDISCIPLINARY GRADUATE SCHOOL
NANYANG ENVIRONMENT & WATER RESEARCH INSTITUTE**

2019

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CARBONISATION OF DURIAN SHELL WASTE**

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Interdisciplinary Graduate School

Nanyang Environment & Water Research Institute (NEWRI)

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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J.R.A. Supuli Jayaweera

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

2019/07/29

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Date

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Prof. Ng Wun Jern

Authorship Attribution Statement

This thesis contains material from 2 papers published and 1 paper under revision in the following peer-reviewed journals in which I am listed as an author.

Chapter 3 is published as Jayaweera, S., Ke, Y., Hu, X. and Ng, W. J. Facile preparation of fluorescent carbon dots for label-free detection of Fe^{3+} , Journal of Photochemistry and Photobiology A Chemistry 2018, DOI: 10.1016/j.jphotochem.2018.10.052.

The contributions of the co-authors are as follows:

- Dr Yin Ke, Prof Hu and Prof Ng provided advice in the initial project direction.
- I designed the study and performed all the laboratory work using facilities at NEWRI, School of Civil and Environmental Engineering and School of Materials Science Engineering at Nanyang Technological University.
- Dr Ke, Prof Hu and Prof Ng assisted in improving the discussion section including assistance in interpreting colour spectroscopy data of the carbon dots.
- I prepared the manuscript drafts. The manuscript was revised by Dr Yin Ke, Prof Hu and Prof Ng.

Chapter 4 is published as Jayaweera, S., Ke, Y. and Ng, W. J. Nitrogen-doped durian shell derived carbon dots for inner filter effect mediated sensing of Tetracycline and fluorescent ink, Journal of fluorescence 2018, DOI: 10.1007/s10895-018-2331-3

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- Dr Yin Ke and Prof Ng provided advice in the initial project direction.

- I designed the study and performed all the laboratory work using facilities at NEWRI, School of Civil and Environmental Engineering and School of Materials Science Engineering at Nanyang Technological University.
- I prepared the manuscript drafts. The manuscript was revised by Dr Yin Ke and Prof Ng.

Chapter 5 is published as Jayaweera, S., Ke, Y., Hu, X. and Ng, W. J. Fluorescent N/Al co-doped carbon dots from cellulose biomass for sensitive detection of Manganese (VII), Journal of fluorescence 2019, DOI: 10.1007/s10895-019-02452-7

The contributions of the co-authors are as follows:

- Dr Yin Ke, Prof Hu and Prof Ng provided advice in the initial project direction including developing new doping methods.
- I designed the study and performed all the laboratory work using facilities at NEWRI, School of Civil and Environmental Engineering and School of Materials Science Engineering at Nanyang Technological University.
- I prepared the manuscript drafts. The manuscript was revised by Dr Yin Ke, Prof Hu and Prof Ng.

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Date

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J.R.A. Supuli Jayaweera

Abstract

Carbon dots (CDs) are an emerging nanomaterial that has been used in multidisciplinary areas of energy, environmental and medical fields as a result of its low toxicity, stable and tunable photoluminescence, aqueous solubility and high biocompatibility. In recent years developments in CDs using biomass has gained attention due to the lower cost, high availability and environmentally friendly nature of the latter. In this report durian shell waste (DSW), a lignocellulosic biomass is used to synthesize high fluorescent CDs. Generally, pure cellulose based CDs exhibit poor photoluminescence. However, it is hypothesized that the naturally present oxygen and nitrogen groups in DSW can contribute to the fluorescent enhancement and even provide necessary anchoring points for external doping agents. Thus, this study had aimed to develop a facile synthesis method to convert DSW to high fluorescent CDs, conduct an extractive analysis to identify the various functional groups present in DSW and evaluate the contribution from these functional groups to the photoluminescence, introduce existing and novel dopants to evaluate the effectiveness of these dopants to the optical properties of CDs and finally use the synthesized CDs as a sensor to detect aqueous pollutants.

Based on the results, a facile one pot hydrothermal method was developed to produce CDs from DSW which showed a quantum yield (QY) two times that of pure cellulose. Through the extractive analysis, it was identified amino and carboxylic acids were pivotal to the higher fluorescence. DSW has a higher response to amino groups and this was subsequently used to develop nitrogen

doped CDs with a QY of 12.9%. Moreover, doping DSW with nitrogen-metal mix subsequently yielded a QY of 28.9%, which was one of the highest recorded cellulose biomass QYs reported from a one pot hydrothermal technique. The CDs were successfully used as sensors for Fe^{3+} , Mn^{7+} ions and the antibiotic tetracycline in aqueous systems. Based on the sensitivity and selectivity tests, CDs showed high selectivity for the targeted species and good linear models for Fe^{3+} , Mn^{7+} and tetracycline were developed with a lowest detection limit of 128 nM, 46.8 nM and 75 nM respectively. The sensing performances of DSW based CDs showed better sensitivity compared with the current fluorescent probes. The mechanisms governing the sensing were further explored. To validate the CDs sensing capabilities, the sensors were applied in real water systems to detect the targeted analyte and the results exhibited good recoveries with acceptable standard deviations.

It could be concluded DSW has the potential to be used as a carbon precursor for CD synthesis. The resulting material can be used as an efficient fluorescent probe to detect aqueous pollutants.

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Abbreviations

DSW	Durian shell waste
CD	Carbon dots
NCD	Nitrogen doped carbon dots
PL	Photoluminescence
HMF	Hydroxy methyl furfural
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
AAS	Atomic absorption spectroscopy
ICP-MS	Inductive coupled plasmon mass spectrometry
AFS	Atomic fluorescence spectroscopy
CA	Citric acid
DAN	Diaminonaphthalene
HTC	Hydrothermal carbonisation
DSSC	Dye sensitized solar cells
PEI	Polyethylenimine
LEDs	Light emitting diodes
EL	Electroluminescence
AIQ	Aggregation induced quenching
PVA	Polyvinyl alcohol
QY	Quantum yield
DI	Deionized
FE-SEM	Field emission scanning electron microscopy
MY	Mass yield
LOD	Limit of detection
TOC	Total organic content
TN	Total nitrogen
RSD	Relative standard deviation

IC	Inorganic Carbon
HPLC	liquid chromatography
MS	Mass spectroscopy
TC	Tetracycline
FTIR	Fourier transform infrared spectroscopy
TEM	Transmission electron microscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray Powder Diffraction
TCSPC	Time-correlated single-photon counting
Lin	Lincomycin
Amox	Amoxicillin
Amp	Ampicillin
Str	Streptomycin
Sulf	Sulfanilamide
Chlo	Chloramphenicol
IFE	Inner filter effect
FRET	Förster Resonance Energy Transfer
MNI	Mean Normalized Intensity
NIR	Near Infrared

Chapter 1 Introduction

This chapter presents an overview of the research background including a brief outline of carbon dots (CDs) and Durian shell waste (DSW), an outline of the research problem that motivated this study, definition of the objectives, scope of the thesis followed by a discussion on the significance of the study. Finally, the chapter concludes with an outline of the upcoming chapters.

1.1 Research Background

Fabrication and use of carbon materials has a history of over 3000 years, starting with ink and pigments. From thereon, development of carbon structures has grown significantly targeting numerous applications. With the discovery of fullerene and carbon nanotubes, the versatility of carbon material has further expanded into the fields of energy and environment sectors [1]. Carbon nanomaterials are a novel form of carbon that has gained attention over the years owing to the unique combination of mechanical, chemical, optical, thermal and electrical properties [2]. Thus, they have been used in different fields of environmental, biomedical and energy sectors as materials for catalyst support, fuel cells, drug delivery and gas storage [2, 3]. Carbon dots (CDs) are a type of carbon-based nanomaterials in the range of 2-10 nanometers that have gained interest due to their physicochemical properties, such as tunable photoluminescence and high biocompatibility [4, 5]. The photoluminescence based applications are expected to reach a market of \$5.69 billion by 2022 [6]. Although CDs have shown good photoluminescence, traditional practice is to use quantum dots. These quantum dots are primarily composed of cadmium selenide (CdSe), zinc sulphide (ZnS) and lead sulphite (PbS) nanocrystals. In addition to the direct raw materials, the synthesizing techniques of quantum dots involve chemical vapour decomposition, arc discharge and laser ablation methods which utilize catalysts comprising of heavy metals like cobalt, iron, nickel and titanium [6, 7]. Thus, synthesis of such nano structures can involve toxic and/or costly materials and harsh operational conditions. However, with the strict regulatory ban on the use of heavy metals in the consumer products in European market has made major QD producers like Nanoco, Nanosys, NN labs and Quantum Materials Corporations towards cadmium free QDs and using low toxic

materials like carbon/graphene in their products [6]. Therefore, developing high quantum yield CDs has become very important.

Apart from the tunable photoluminescence and high biocompatibility, studies have proven CDs to be versatile material with easy functionalization and low toxicity. With these properties, CDs have shown potential for application in fields such as optical sensors, photovoltaics, catalysts, bio-imaging, and optoelectronics [8]. Nevertheless, irregular morphology, low PL quantum yield, poor size control and time consuming post fabrication purification steps still challenge the full scale use of CDs in commercialized applications [9]. However, there have been an increasing number of patents on producing CDs with uniform size distribution and solution chemistry methodologies that strongly indicate the movement of CDs towards translational research [10-13]

To address the challenges associated with sustainable precursor materials, studies have been done on synthesizing carbon structures from biomass. Biomass is referred to the organic plants or plant base matter generated via photosynthesis using water and CO₂ [14, 15]. With an annual generation of over 104.9 petagrams of carbon from biomass, producing carbon structures from it can be regarded as part of a natural carbon cycle with the added benefit of a low cost, abundant and renewable precursor [1, 15, 16]. Moreover, biomass coupled with a green synthesis technology can significantly contribute to reducing greenhouse gas emissions and avoid using harmful chemicals. Primarily, biomass is composed of cellulose, hemicellulose and lignin with a content range of 40-60%, 20-40% and 10-25% respectively [17]. Thus, the carbon rich nature of the biomass has attracted its use as a precursor for carbon materials like biochar and activated carbon [16].

CDs have been generated using bulk carbon materials like graphite rods as well as from natural and synthetic molecules. The most common synthesis chemicals include citric acids, citrate salts, chitin, acrylic acid and polymers coupled with various amines as the nitrogen source [18]. Natural sources of carbon used for CDs production include egg shell membrane [19], prawn shells [20, 21], banana [22], lotus root [23], coriander leaves [24], rose petals [25], aloe [26], bombyx mori silk [27], garlic [28], and rice husk [29].

Cellulose is a linear polysaccharide consisting of β linked D-glucose units [30]. It is the most abundant macromolecule in nature, with 50% of the natural biomass represented by cellulose. Thus, use of cellulosic biomass for CD production has multiple advantages. First, the low cost, high availability, high biocompatibility, low toxicity and eco-friendly nature of cellulose improves the environmental and economic aspects of CD production. Secondly, cellulose is a rich source of oxygenated functional entities including hydroxyl and ether groups which could provide structural and optical benefits to the CDs [30]. Thirdly, most biomasses contain heteroatoms (e.g. N, S) in the form of extractives. Heteroatoms doping and surface functionalization are important features in tuning the carbon dots for enhanced photoluminescence (PL) and thus, using a natural cellulose derivative with the presence of such dopants provide additional advantages over pure chemicals [31, 32].

1.2 Research Problem

Durian (*Durio zibethinus*) is a tropical seasonal fruit that is popular in Asian countries with an annual harvest of 1.4 million tons [33]. With the rising demand for durians, there is a significant waste management challenge since nearly 50% of the fruit mass

is thrown away as shell waste [34]. From the review of fruit and vegetable waste generation, durian has the highest wastage by mass percentage with a 70% whereas bananas (35%) , grapes (20%), mango (45%), tomato (20%), pineapple (33%) and potato (15%) were considerably lower [35]. Generally, many agro wastes can be used to produce biogas through anaerobic digestion. However, the high lignocellulose content in durian shell can be difficult to anaerobically degrade. This creates a nutrient imbalance for the microorganisms and at the same time the nitrogen present in durian shells can inhibit the anaerobic digestion process [36]. In the past, there have been attempts to utilize durian shell to produce novel materials like polysaccharide gels and dietary fibers to be used in the pharmaceutical and food processing industries [33]. However, these developments typically involved complex multi-step treatments and the use of expensive chemicals which had impeded large scale synthesis and commercialization. However, producing CDs from durian shells has an inherent advantage because of the shell's composition. Eventhough the bulk of durian shell waste consists of lignocellulose (~90%), the rest is composed of extractives which includes phenolic, carboxylic and amine groups [37, 38]. Thus, it is expected that these functional groups can produce CDs with better quality with boosted photoluminescence. Moreover, developing a successful method and dopants for high quality CDs can potentially lead to exploitation of other lignocellulosic biomass for CD production. Examples of these can possibly include processing wastes from sago and crude palm oil production.

Herein, durian shells are used in a facile synthesis process to produce carbon dots (CDs) which add value to this agro-waste via possibility of sustainable large scale production. The generated CDs could be used as an optical sensor to detect pollutants in water. The use of cellulose in durian shells as precursor for carbon dots synthesis has a potential

cost benefit [4, 39]. However, cellulosic materials result in lower photoluminescence yields typically less than 5% [4, 39-41]. Photoluminescence (PL) is a key characteristic in CDs which define the quality and applicability of CDs. PL depends on factors such as the quantum confinement effect governed by the size of the particle or surface effect governed by surface traps, edge states and heteroatoms [42]. Thus, functional groups and surface defects on the CDs have a significant impact on the luminescent characteristics of CDs [43]. To address this, cellulosic substrates are either pre/post treated with nitrogen/sulfur compounds - e.g., Urea, Ammonium Carbonate, Sulfuric Acid, and Nitric Acid [39]. Thus, the first challenge in this study is to produce CDs with higher quantum yield compared with pure cellulose. It is hypothesized that it would be possible with the naturally present heteroatoms and functional groups in durian shells. Then common doping agents as well as novel dopants were also investigated to evaluate their effect on durian shells based CDs. Unlike previous studies associated with durian shells, a facile method had to be developed with fewer chemicals and procedures to increase economic and environmental viability

1.3 Scope and Objectives

In this study, durian shells are used in a one-step hydrothermal carbonisation (HTC) process to synthesis CDs. HTC is a facile synthesis process that uses low temperatures profiles (<250°C). The overall objectives of the study are outlined below;

- ❖ To produce carbon dots from DSW using hydrothermal carbonisation method and selection of optimum temperatures and residence times by comparing the quantum yield and mass yield of the DSW derived CDs and cellulose based CDs.

- ❖ To extract DSW extractives and investigate the components with chromatography and mass spectroscopy techniques. Categorize these components based on the active functional groups and evaluate the effect on each group on the CDs' photoluminescence characteristics.
- ❖ To investigate the effect of known and novel dopants on improvements to the chemical, physical, and optical properties of CDs while using cellulose based CDs as the benchmark.
- ❖ To apply the synthesised CDs as a ratiometric sensor to detect pollutants in water. To explore the sensing mechanism in detail. To model the sensitivity and selectivity towards the targeted analyte based on a linear model and validate the model with actual water.

1.4 Significance and Contributions

Advanced functional nanomaterials have been synthesized using high purity chemicals. However, with the increasing focus on environment friendly practices renewable resources like biomass have become increasingly important. DSW is a low cost, abundant resource. DSW also contains approximately 10-11% of extractives which are a combination of aldehydes (e.g. HMF), water soluble starch residues, carboxyl groups rich pectins, flavonoids, carotenoids and proteins [15-17]. The oxygen-rich functional groups in DSW can help create in the CDs edge and surface defect states for higher photoluminescence. Furthermore, heteroatoms including nitrogen create emissive trap states for photoexcited electrons, which modify the band gap energy and this can change the optoelectronic properties [44]. Thus, this study seeks to utilize the unique DSW composition to enhance CD performance. This study's new dopants significantly

increased the quantum yield, and this provided possibility for high quality CD production from other lignocellulosic biomass in future.

The synthesized CDs could be used as metal ions/antibiotics sensors in water systems. The current methods for detection involve time consuming atomic absorption spectroscopy (AAS) or inductive coupled plasma mass spectrometry (ICP-MS) or liquid chromatography (LC) techniques [45]. CDs present possibility for fast, selective and sensitive detection of pollutants in waterbodies over the preceding methods [46]. Given CDs' water solubility, dispersibility and non-toxicity it further adds more value over conventional techniques.

Inappropriate disposal of DSWs can cause adverse environmental effects as it contaminates receiving waterbodies and uses up incinerator or landfill capacities. In Singapore, disposal of durian shells is an economic burden on durian vendors with the seasonal disposal charges [47]. In major durian producing countries like Malaysia, Thailand, and Indonesia, the waste disposal is primarily by landfilling and open dumping [48-50]. Most of these sites are poorly maintained which escalates the environmental pollution. Currently, to mitigate the challenges associated with solid waste, the Malaysian government intends to provide tax incentives for those who adopt green waste initiatives including waste recovery [51]. Furthermore, China, the largest importer of durians is moving towards sorting waste to reduce the difficulties in landfill based waste disposal [52]. Thus, it is evident that countries are striving for new methods to treat waste and this study proposes a simple methodology for the production of a value added product from DSW which reduces the economical and operational burden of waste disposal.

1.5 Thesis Outline

A brief outline of this thesis is presented in this section.

- ❖ Chapter 1 introduces the thesis by discussing the background and motivation for this research. Then the research challenges are identified which sets the scope and the objectives. Finally, the contribution and significance of the thesis are discussed briefly. The chapter concludes with the sectional overview of each chapter.
- ❖ Chapter 2 is a detail literature review on the carbon dots beginning with structures and the probable mechanisms developed so far to explain the photoluminescence of CDs. Then different synthesis routes for CDs are discussed followed by multidisciplinary applications of CDs. The final section of the literature review is completed with a brief overview of cellulose based CDs, an introduction to durian shell waste and finally identifying research gaps and problems in the literature.
- ❖ Chapter 3 investigates the methodology and the optimization of CDs production from DSW and then analyze the extractives present in DSW which will be further evaluated in terms of the effect to the PL properties. A detail discussion of the characterisation of the CDs and application of synthesised CDs for detection of Fe^{3+} ions are also evaluated.
- ❖ Chapter 4 investigates the effectiveness of nitrogen doping on DSW based CDs. The CDs are characterised for its structural, chemical and optical properties followed by the application and mechanism associated with the detection of antibiotics in water as well as the performance of the CDs as a fluorescent marker.

- ❖ Chapter 5 uses a novel dopant mix consisting of a metal co-dopant system to enhance the PL of DSW based CDs and discusses the characteristics of the synthesised CDs in detail. Furthermore, these doped CDs are applied as a ratiometric sensor to detect Mn^{7+} water.
- ❖ Chapter 6 presents a summary of the thesis and discusses in brief of the further developments and future directives that elevate the significance of the thesis.

Chapter 2 Literature Review

Carbon dots (CDs), first discovered in 2004, is a recent member of the functional nanomaterial family of fullerene, nanotubes and graphene. In this chapter, a concise review is done on structure and the classification of CDs followed by the different routes adopted so far to synthesis CDs and their advantages and limitations. Furthermore, the review discusses the possible mechanisms developed to explain the photoluminescence, the most revered characteristics of CDs. Then the recent trends in different applications of CDs including sensing, imaging, nanomedicine, photocatalysis, photovoltaics and optoelectronics are discussed along with the further developments. Then an overview of studies in synthesizing CDs from cellulose biomass is conducted followed by the currents trends and challenges associated with treating durian waste. Finally, the review is concluded highlighting the challenges and future directives of CD synthesis from biomass.

2.0 Introduction

Zero-dimensional Carbon dots (CDs) is a recent addition to the functional nanomaterial family of fullerene, nanotubes, nanodiamonds and graphene [42, 53]. These quasi-spherical particles, generally in the size of 2-20nm, were first discovered in 2004 during purification of single walled carbon nanotubes synthesized via arc-discharge method [54, 55]. Since then the studies related the CDs have been exponentially increasing primarily due to the innate properties of CDs including tunable photoluminescence, chemical inertness, low cytotoxicity, aqueous solubility, high biocompatibility, resistance to photobleaching and facile synthesis techniques. These characteristics enabled CDs to be a promising alternative for the conventional heavy metal based semiconductor quantum dots which are currently in use.

2.1 Structure and classification of Carbon Dots

The structure of CD is highly depends on the source material as well as the processing method [53, 56]. Three distinct regions based on the photoluminescence emission can be identified in a typical CD as shown in Figure 2-1a. At the center is the CD core which consists of a graphene like sp² hybridized carbon atoms [57]. As illustrated in Figure 2-1b, variations of the core sp² structure have further classified carbon dots into graphene quantum dots, graphite CDs or amorphous CDs [56].

Graphene is a two dimensional material with a single layer of carbon atoms sharing sp² hybrid bonding while the core of the graphitic carbon dots is composed of layers of sp² hybridized carbon stacked upon each other. Apart from the crystalline graphitic cores, few groups have reported carbon dots with very high level of N doping that their core consists of carbon nitride structures with in graphitic or β -crystalline arrangement [56].

On the other hand, the amorphous carbon is one of the most popular carbon dot structure and the focus of this study hereon. This core consists of a mixture of carbon to carbon graphene type sp^2 hybridisation dispersed in a diamond type sp^3 hybridized carbon structure in varying proportions that result in structural disorder [53, 56]. In general, these amorphous CDs are quasi spherical with a size less than 10 nm and a height of 0.5 to 5 nm [58]. The lattice distance between the layers are generally around 0.34 nm [58, 59].

Figure 2-1: (a) Structure of carbon dots and (b) Structural core analysis of the carbon dots

Aside from the core there are two distinguishable regions in the CD structure named surface state and the molecular state. The surface state is located at the periphery of the sp^2 hybridized CD core and composed of heteroatomic functional groups like hydroxyl, carboxyl, carboxylate, amine, amide and sulfur groups [60]. The molecular state constitutes small molecular chromophores that acts as an organic dye. These molecules may or may not be covalently attached to the carbon core [61] and are basically residual moieties that get attached the CD surface when the precursor undergoes carbonization and dehydration reactions [60]. These three regions distinctly contribute to the

photoluminescence of CDs and as such modification of each region can achieve a significant improvement to the overall optical performance. In addition, polar groups that decorate the carbon dots impart carbon dots with aqueous solubility and enable subsequent functionalization with other organic, inorganic, polymeric compounds [53, 58, 59]. Generally, the fabrication of CDs involve oxidation steps that naturally introduce oxygen containing moieties like carboxyl, carbonyl and hydroxyl groups to the CD surface [62]. However, certain literature has indicated for very high photoluminescence, CDs may have to be passivated with more complex molecules like polyethylene glycol or polyethyleneimine [56].

2.2 Mechanism of Photoluminescence (PL)

Several mechanisms have been proposed over the years including quantum confinement effect, surface states or defects, molecular states and crosslinked enhanced molecular effect to explain the PL of the CDs and an unanimous method is yet to be decided [53, 63]. The following section briefly explains the most commonly accepted mechanisms.

2.2.1 Quantum confinement effect

The quantum confinement effect is observed when the size of the particle is too small that it confines the electrons geometrically and the electrons adjust its energy to respond to the decreasing particles size. Further, the decreasing number of overlapping orbitals leads to discrete energy levels as opposed to the continuous energy bands present in bulk material. Thus, the energy gap is determined by the size and shape of the particle which directly effects the PL [64]. Further, variations of the particle size will lead a broad spectrum of emission [42]. Several studies have published work corresponding

to range of fluorescence emission that coincides with the size of the particles [64, 65]. Fan and coworkers have produced multicolor fluorescent CDs by controlled carbonization of citric acid (CA) and diaminonaphthalene (DAN) using solvothermal method (Figure 2-2a). The solutions emitted blue, green, yellow, orange and red colours under UV light ($\lambda_{\text{ex}} = 365 \text{ nm}$) which are in line with the increasing particle sizes of 1.95, 2.41, 3.78, 4.90 and 6.68 nm, respectively (Figure 2-2b) [64]. Similarly, Lee and coworkers have used electrochemical method to synthesise blue, green, yellow and red emitting CDs which are closely related to the size of the particles [65].

Figure 2-2: (a) Preparation of MCBF-CQDs from blue to red by solvothermal treatment of CA and DAN and (b) Photographs of MCBF-CQDs under daylight (left) and fluorescence images (right) under UV light (excited at 365 nm). Adopted from [64]

Although, quantum confinement is one of the widely accepted mechanism to explain the fluorescence mechanism of CDs, multitude of works have been published that contradict with the size controlled emissions. For example, Hueso et al. flash pyrolyzed citric and EDTA to produce undoped and nitrogen doped carbon dots which have similar blue emission at 420 nm irrespective that their average sizes are different [66]. Dai et al proposed that the emission could be due to the isolated sp² clusters present in the sp³ carbon matrix that gives rise to the π to π^* electron transition. If the size of the sp² cluster remains similar, the emission would be independent from the size of the nanoparticle [67]. Currently, this remains the highly accepted mechanism to explain the excitation independent fluorescence behaviour.

In addition to the above, many studies in literature dictate PL emissions of CDs are closely associated with a combination of above mentioned aromatic sp² effect together with surface state of the CDs [66, 68-70].

2.2.2 Surface State Emissions

Surface state of CDs refer to the surface traps associated with functional groups on the carbon dots and defects. Figure 2-3 depicts the Jablonski diagram for electronic state and transfer of electrons between the bandgap of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels. On absorbance of a photon, HOMO electrons will transfer to the LUMO energy band which is followed by the non-radiative vibrational relaxation process. Vibrational relaxation is where the energy in electrons is dissipated by converting to other vibrational modes as kinetic energy. It is a fast transition and generally electrons will not change the core electronic level [71]. After vibrational relaxation, the electrons will emit energy as photons and

return to HOMO energy level. This is known as fluorescence and it is a slow process on the order of 10^{-9} to 10^{-7} seconds. Generally, carbon dot surface contains abundant amounts of oxygen functional groups like -COOH, -C=O, -C-O-C, and other nitrogen, sulfur groups subjected to the precursor material and synthesised routes. Surface defects in π electronic conjugations are caused when the sp^2 hybridized carbon domain are disrupted with sp^3 structures [72]. These surface states introduce many energy levels between the HOMO and LUMO core states and multiple transitions which result in wide emission peaks [73]. The presence of surface states alters the fluorescence properties by changing the bandgap of the CDs and thus, controlled functionalization was one of the frequently adopted method to get a wide array of fluorescence emissions from CDs [72, 74].

Figure 2-3: Simplified Jablonski diagram for surface state mediated fluorescence

To elaborate the above principle, Xiong and his group synthesised CDs with eight different emission colours (Figure 2-4) ranging from blue to red from hydrothermal carbonisation of Urea and p-phenylenediamine and then using a silica column chromatography apparatus to separate the different CDs based on its polarity [74]. Further, structural characterisation confirmed that both carboxyl content and degree of

oxidation directly affected the PL by creating surface defects. Higher level of surface oxidation caused a red shifted emission. Further, Zeng et al produced green emitting CDs from citric acid and urea where they have concluded oxidized -C=O groups were responsible for green emission and the blue emission was related to the surface hydroxyl groups [73].

Figure 2-4: (A) One-pot synthesis and purification route for CDs with distinct fluorescence characteristics, (B) Eight CD samples under 365 nm UV light and (C) Corresponding PL emission spectra of the eight samples. Adopted from [74]

Eventhough most of the CDs have shown pH independent emissions, presence of functional groups can have a net effect on the fluorescence of CDs. For example, Mandal and Basu produced a pH sensitive CDs where the change in quantum yield and emission peak was correlated to the pH dependent deprotonation of -COOH and phenolic -OH groups [57]. Further, Zhu and his group identified the pH dependent

behaviour of hair fiber based CDs was due to the presence of -COOH and -NH₂ groups [75]. These functional groups caused the CDs to show properties equivalent to amphoteric amino acids with fluctuating isoelectric points and dissociation constants which modulated the emission of CDs based on pH.

It is evident that that surface state directly effects the fluorescence properties and raw CDs could contain defect states that contribute to excitation dependent emissions, non-radiative recombinations and makes CDs sensitive to external conditions [42, 68]. Thus, surface passivation, a surface functionalization technique, was developed where a thin passivating layer of organic (e.g. organ silane and polyethylene glycol), polymeric, inorganic or biological materials around the CD surface was applied which imparts CDs with high quantum yields, excitation independent fluorescence emissions and photostability [42, 76]. Overall, it can be identified that surface functionalization plays a significant role in the optical and physical characteristics in CDs.

2.2.3 Molecular State Emissions

Molecular state emission arises when organic fluorophores are used as the precursor material for the CD synthesis. These molecules may or may not be covalently linked with the main carbogenic structure of the CDs or else they can couple with the edge carbon atoms or functional groups of the CDs leading to $n-\pi^*$ or $\pi-\pi^*$ transitions [54, 61, 77, 78]. This phenomena was first identified by Giannelis and his coworkers, when they developed CDs which emitted single, excitation independent PL behaviour with 50% quantum yield [79]. This emission is attributed to the amide containing fluorophores that were present in the carbogenic core. However, with increasing

pyrolytic temperature, most of the fluorophores were consumed to form the carbogenic core resulting in reduced quantum yield and red shifted emission.

Jamshidi and coworkers extracted the emission spectra for each emission centers from CDs synthesised from pyrolyzing citric acid and ethanolamine [77]. As shown in Figure 2-5, at low temperatures, cyclization and polymerizations of materials produced polymeric like CDs incorporated with fluorophores to yield high fluorescence. When the temperature is increased, the dehydration reactions form complex aromatic structures within the polymeric structure which exhibited different emission peaks. Further carbonization caused the aromatic compounds to convert to the carbogenic core which produced CDs with lower quantum yields. Apart from temperature effects, few studies have identified similar results by increasing the reaction time [77, 80].

Figure 2-5: Fluorescence spectrum related to the molecular, aromatic and carbon core states with increasing temperatures. Adopted from [77]

Although above mentioned mechanisms serve as the most recognized models to explain the CDs fluorescence behaviour, it is still under debate and many CDs exhibit emissions arising from combination effect of multiple models which make it a complex process to unravel. Thus, development a proper model requires further investigations in the future.

2.3 Synthesis Process

There are many synthetic routs for the CD formation and the methods can be broadly categorized in to two – top down approach and bottom up method as shown in Figure 2-6. The former is cleaving the large carbon structure like fullerene, carbon tubes or graphene in to smaller size while the latter is assembling small molecules like glucose and fructose under different operational conditions to form the carbon dots [54, 58, 62, 81]. Whichever the selected pathway, it is important to note that that the synthetic route affects the size, functional groups and colloidal stability and thus, directly governs the physio-chemical and optical properties of CDs [53, 81].

Figure 2-6: Representation of the possible synthesis methods to prepare carbon dots.

Adopted from [82]

2.3.1 Top- Down approach

Top down approach generally takes harsh physical or chemical conditions to reduce graphite powders, multiwall carbon nanotubes, graphene, graphene oxide sheets, carbon fibers, soot and other materials that has perfect sp² structure in to CDs [58, 81]. The most common techniques involve arc discharge, laser ablation, acid oxidation and electrochemical oxidations which have been discussed in detail in the following section. However there have been few reports of solvothermal methods [83, 84], chemical exfoliation [85], reactive ion etching [86] and photo-Fenton reactions [87] that were utilized to synthesis CDs. Overall, top down methods are generally complicated and even environmentally hazardous and may not be suitable for large scale synthesis [58].

2.3.1.1 Oxidation

In this method, strong oxidizing agents are used to breakdown carbon structures into nanoparticle levels. Mittal and Kushwaha produced CDs by refluxing MWCNTs with concentrated HNO₃ and H₂SO₄ acids [88]. As shown in Figure 2-7, during the oxidation, the surface and the tip of carbon tubes were oxidized to form carbonyl, carboxylic, sulfonic and nitro groups. With increasing time more layers underneath the surface layer got oxidized leading to bending and buckling of the nanotubes. Finally, the carbon tubes collapsed into forming the CDs. Similarly, lampblack particles [89], carbon nano-powder [90] and carbon black [91] have been oxidized by refluxing with nitric acid. CDs emission wavelength can be modulated by differing the carbon source and the oxidation condition [53, 59].

Figure 2-7: Proposed mechanism for the formation of carbon nanoparticle from over-oxidation of multiwalled carbon nanotubes. Adopted from [88]

2.3.1.2 Laser ablation

During laser ablation, the bulk carbon source is placed in a liquid and a pulse laser beam is focused on the target source at which point the focal point get heated, melted, vaporized and generate a plume of nanoparticles [92]. The particles are suspended in the liquid medium for easy separation and generally, this method is considered to be faster and simpler [92, 93]. Du et al, conducted the laser ablation technique on graphite powders dispersed in three different solvents and reported the emission peaks of the CDs samples were located at different wavelengths, even though the size distribution of the particles are same [94]. Similar observations were made by Koshizaki et al when they produced CDs from nano-carbon material [95]. Both studies reported that CDs made in water, did not emit any fluorescence and suggested ligands generated in the organic solvents were responsible for higher PL by functionalization and passivation the surface of CDs. Moreover, Du and his group reported that increasing molecular weight of the solvent caused a red shift in the wavelength [94]. Thus, the fluorescence properties of CDs under laser ablation is heavily controlled by the selection of the solvent.

2.3.1.3 Electrochemical release

The electrochemical method is a chemical cutting process of a bulk carbon source like graphite rod, carbon nanotubes, carbon paste or carbon fiber in an electrolyte solution [53, 96]. Different electrolytes can be used including ionic liquid, acetonitrile containing tetrabutylammonium perchlorate and NaH_2PO_4 [96]. The fluorescence properties, size, and surface states of the CDs can be easily manipulated by controlling the electrochemical operational parameters like electric field, concentration of the electrolyte and diameter of the electrodes and temperature [53, 96, 97]. Different electrode configurations have been studied previously. For example, Liu and his group synthesised CDs from three electrode system where Graphite, platinum foil and Ag/AgCl were used as the working, counter and the reference electrodes, respectively and a NaOH/Ethanol mix was used as the electrolyte (Figure 2-8a) [96]. They identified that higher potential leads to larger CD size and the alcohols and -OH groups play a key role in CD synthesis. Additionally, Long et al synthesised nitrogen doped CDs from a two electrode set up with two platinum sheets employed as working and the auxiliary electrodes while a mix of pyrocatechol and ethanediamine in water as the electrolyte [97]. Given the ability to use the electrolyte as the precursor material for CD synthesis facilitates more controlled and low cost synthesis method for CD production.

2.3.1.4 Arc Discharge

During arc discharge, two electrodes are mounted inside a liquid/gas chamber (Figure 2-8b) where the anode is the carbon precursor and the cathode is generally a graphite rod [98]. Once a constant current is maintained through the electrodes to get a non-

fluctuating arc, the current generates a plasma of very high temperature which sublimates the carbon precursor. The vaporized carbon aggregates in the gas phase and moves towards the cathode to be deposited [98, 99]. Generally, this is a commonly practiced method to produce CNTs [98] and was used to produce CDs for the first time where the presence of CDs was identified in the crude soot by Xu et al [55, 100]. They later separated the CDs by oxidizing the soot and conducting gel electrophoresis. Although the oxidizing of soot renders the CDs with higher oxygen content, the generated soot from arc discharge method contains impurities which are of complex nature and thus poses challenges in the subsequent separation [101].

Figure 2-8: (a) Schematic illustration for CQDs generation via electrochemical oxidation of graphite electrode in alkaline alcohols and (b) Schematic of an arc discharge setup (right). Adopted from [96] and [98]

2.3.2 Bottom-up approach

Bottom up approach can be considered as the most commonly used technique to synthesise CDs where molecular precursors like carbohydrates, citrates, biomaterials, cellulose, polymers composites are arranged under different synthetic routes that

include pyrolysis and microwave assisted/ hydrothermal carbonisation [53, 54]. Further, these methods are facile, low cost, highly efficient and the properties of CDs can be easily manipulated by controlling the operational conditions which makes it suitable for large scale synthesis [55, 58].

2.3.2.1 Microwave Irradiation

This is a rapid synthesizing method where the carbon source is dissolved in water or a buffer solution and placed inside microwave for several minutes. Compared to other methods it is highly convenient and reactions can be completed without a temperature gradient using even a domestic microwave oven [53, 102]. However, in microwave irradiation, heat is generated by friction between molecules under an electromagnetic field which is directly related with its dielectric constant [103]. When biomass compounds are used, amorphous regions will be more reactive compared to the crystalline regions [104]. Thus, limitations can arise related to the complex feedstock composition of the biomass and challenges in controlling the irradiation power affects reproducibility [102]. Nevertheless, microwave irradiation has been used in recent years to produce CDs from different biomasses as summarized in table 2-1.

Table 2-1: Microwave assisted CDs from biomass sources

Biomass Type	Reaction Parameters	QY	Emission Wavelength (nm)	Application	Ref.
Wool	200 °C for 60 min	16.3%	450 nm	Sensing Glyphosate	[105]
Lotus Root	800 W for 6min	19.0%	435 nm	Sensing Hg ⁺ and cell imaging	[23]
Goose Feather	180 °C for 40 min	17.1%	425 nm	Sensing Fe ³⁺	[106]
Silk fibroin	200 °C for 4 hrs	20.0%	460 nm	Bioimaging	[107]
Kelp	200 °C for 1.5 hrs	23.5%	450 nm	Sensing Co ²⁺	[108]
Algal Blooms	600 W for 5.8 min	13.0%	438 nm	Cell imaging	[109]
Sesame Seeds	800 W for 15 min	8.02%	440 nm	Sensing Fe ³⁺	[110]

2.3.2.2 Hydrothermal Carbonisation (HTC)

HTC is cheap, environmentally friendly and nontoxic method and one of the most commonly used technique to fabricate CDs [59]. Additionally, it has facile instrumentation requirements, high atom economy and the possibility for large scale synthesis [111]. Simply, the solution of organic precursors is reacted under autogenous pressure in a sealed hydrothermal reactor at a controlled temperature and time and CDs can be obtained by purifying the resulting solution [53, 59, 111]. The major limitation of HTC in CD synthesis is poor control of size and thus, purification plays a key role in obtaining a monodisperse CD solution [111]. These purification methods include filtration, centrifugation, column chromatography and dialysis [112]. During HTC reactions carbon precursors (cellulose/carbohydrates etc) undergo series of reaction starting with hydrolysis where long chain molecules like cellulose are broken down to oligomers, fructose and glucose [113, 114]. These small compounds then follow isomerization, dehydration and fragmentation producing intermediary products like furfurals, carboxylic acids and aldehydes [113-115]. Then, these intermediaries undergo polymerization, condensation, dehydration and aromatization reactions leading to the nuclei formation. Subsequently, nuclei will grow by diffusion and the oxygen/nitrogen groups present in the solution will be linked to the surface forming CDs with a hydrophobic core and a functional groups rich hydrophilic shell [113, 116]. Thus, hydrothermal solution composition, reaction temperature, solvent properties, additives and time can be used to control the particle morphology, grain size, crystalline phase and surface chemistry of the CDs [117]. Table 2-2 summarizes some of the recent developments of CDs from biomass by HTC for different fields of applications.

Table 2-2: Hydrothermal carbonisation of biomass for CD synthesis

Biomass Type	Temp.	Time	Mass Yield	QY	Application	Ref.
Lobster Shells	200°C	6 hrs	0.26%	12.70%	Solar Cells	[118]
Shrimp Shells	180°C	15 hrs	-		Electrocatalyst	[119]
Corn Stalks	160°C	10 hrs	-	7.6%	Fe ²⁺ and H ₂ O ₂ Detection	[120]
Pomelo Juice	200°C	12 hrs	-	18.7%	Cr ⁶⁺ detection	[121]
Shrimp Shells	180°C	15 hrs	5%	-	Electrocatalyst for ORR	[122]
Shrimp Shells	180°C	15 hrs	15%	-	Electrocatalyst for ORR	[123]
Prawn Shells	180°C	12 hrs	18%	-	Nitrite Detection	[20]
Prawn shells	200°C	8 hrs	-	9.0%	Cu ²⁺ Detection	[21]
Fruit Extract	180°C	5 hrs	-	16.0%	Cell Imaging	[124]
Fruit Extract	180°C	5 hrs	-	13.0%	Fe ³⁺ Detection	[125]
Grape Peels	180°C	6 hrs	-	3.1%	Fe ³⁺ Detection	[41]
Goose Feather	180°C	40 mins	-	17.1%	Fe ³⁺ Detection	[106]
Fish Scales	200°C	24 hrs	-	17.08%	ClO ⁻ Detection	[126]
Apple Juice	150°C	12 hrs	-	4.27%	Cell Imaging	[127]
Lime Juice	180°C	7 hrs	-	40.00%	Hg ²⁺ Detection	[128]
Garlic	200°C	3 hrs	-	17.50%	Cell Imaging	[28]
Waste Frying Oil	100°C	5 mins	23.22%	3.66%	Cell Imaging	[129]
Bagasse	180°C	3 hrs	9.30%	12.30%	Cell Imaging	[130]
Milk	180°C	2 hrs	-	12.00%	Cell Imaging	[131]
Rapeseed spent meal	180°C	3 hrs	9.42%	9.20%	Food Packaging	[132]
Orange Peels	180°C	12 hrs	12.30%	36.00%	Photocatalyst	[133]
Bagasse	220°C	1 hr	-	2.70%	Catalyst	[40]
Pomelo Peels	200°C	3 hrs	-	6.90%	Hg ²⁺ Detection	[5]

2.3.2.3 Other methods

Although microwave assisted and HTC are the primarily used bottom up synthetic methods, there have been few other techniques developed using molecular compounds. For example, Kang and his group produced CDs from ultrasonic treatment of glucose solution in the presence of an alkali or acid. The CDs were highly stable with a QY around 7% [134]. Additionally, Tan et al synthesised CDs from sago waste from direct pyrolyzing followed by dissolving the pyrolyzed char in water. The solution was

ultrasonically treated and centrifuged to obtain the final CD solution which emitted blue colour [135].

Top down methods typically require more expensive equipment and supporting facilities as well as requiring higher energy input. The latter can be in the form of heat, electricity or solar [136]. Some top down methods utilize toxic reagents (strong alkali/acids), non-polar organic solvents and stabilizing agents to prevent agglomeration of the nanoparticles [137]. However, top down methods have the advantage of synthesizing CDs with more controlled shape and size. The bottom up approach allows for lower processing temperature and opportunity to influence the composition of CDs on the molecular scale. Further, bottom up methods produce nanostructures with fewer defects and more homogenous chemical composition [136, 138]. Table 2-3 summarizes the drawbacks and advantages of synthesis approaches in relation to CD quality.

Table 2-3: Advantages and Drawbacks of synthesis methods on quality of CDs

Approach	Method	Advantages	Drawbacks	Ref
Top Down Method	oxidation	<ul style="list-style-type: none"> • Provide CDs surface with high carboxyl, carbonyl and hydroxyl groups 	<ul style="list-style-type: none"> • Low photoluminescence • Contaminates removals with time intensive washing and filtration steps • Environmental impact of toxic reagents (strong acid/alkali) 	[137, 139, 140]
	Laser ablation	<ul style="list-style-type: none"> • High-purity particles determined by the purity of the target and ambient media • Control the emission properties through solvent • longer ablation time for synthesis of high smaller-sized nanostructures 	<ul style="list-style-type: none"> • Difficult to control size distribution, agglomeration, and crystal structure • Requirement of stabilizing agents, and various synthetic capping agents • complicated operation and high cost limit 	[137, 141-143]
	Electrochemical release	<ul style="list-style-type: none"> • abundance of raw materials • ease of operation • potential for mass production • low cost setup • Not involving any harsh or toxic chemicals 	<ul style="list-style-type: none"> • Non uniformity in size distribution • Low photoluminescence • Difficulty in purification process 	[144, 145]
	Arc discharge	<ul style="list-style-type: none"> • Nanoparticles have good water solubility • Simple and fast procedure 	<ul style="list-style-type: none"> • Large particle size distribution • Very high temperature process • Separation difficulty of nanoparticles from impurities 	[101, 143]

Bottom up Method	Microwave Digestion	<ul style="list-style-type: none">• High oxygen containing groups on the surface• Low cost setup• Simple, fast and environment-friendly preparation	<ul style="list-style-type: none">• Poor control of the size of particles• Irregularities in crystalline and amorphous regions in biomass effects the reproducibility	[102, 143, 145]
	HTC	<ul style="list-style-type: none">• Easy functionalization of nanoparticles• High water solubility• Facile instrumentation and process• High atom economy• Easy preprocessing of raw materials• Low temperature process	<ul style="list-style-type: none">• Poor control of the size of particles• Impossible to observe the reaction	[111, 146]

2.4 Applications

Tunable photoluminescence, low toxicity, high biocompatibility, aqueous solubility and resistance to photobleaching has rendered CDs to be applied in wider application platforms as shown in figure 2-9.

2.4.1 Sensors

CDs have been widely applied as a fast response, efficient and a selective sensor for a broad range of analytes including cations, anions, small molecules (glucose, thiols), macromolecules (DNA, proteins) and biological compounds (cells, bacteria) [54]. High aqueous solubility, simple instrumentation and the tunability of CDs to resist fluorescence signal variations to temperature, pH, ionic strength and photobleaching has favored the use of CDs over conventional methods involving mass spectroscopy and liquid chromatography.

Figure 2-9: Summary diagram of properties and applications of CDs.

Over the years many theories have been developed to elucidate the interactions between CDs and the analytes. The most recognized mechanisms are;

- I. Photoinduced Electron Transfer (PET): This is a redox reaction where the excited electron in the CDs (donor) are transferred to the analyte (acceptor) and a complex is formed between the donor and the acceptor which comes to the ground state without emission.
- II. Resonance Energy Transfer: When the excited electrons in CDs return to the ground state, it can transfer the energy to the analyte provided the two are kept within a minimal spatial radius and the emission spectra of the CDs overlaps with the analytes' absorption spectra.
- III. Inner filter effect (IFE): When the analytes absorption spectra overlaps with the CDs excitation spectra, portion of the light will be absorbed by the analyte and thereby reducing the intensity of the excited electrons. However, this phenomenon does not change the fluoresce lifetime as opposed to the above mentioned resonance energy transfer.

Different sensor setups have been developed based on the interactions with the analyte. Most widely spread is the fluorescent quenching type where the fluorescence intensity dropped with increasing analyte concentration. As opposed to this some have developed fluorescence enhancement models as well. For instance, Shen et al synthesised chitosan based CDs which detected Ag^+ ions by fluorescence quenching [147] while fluorescence enhanced emission was detected from the dihydric alcohol derived CDs for Ag^+ [148]. Furthermore, some studies have constructed logic gates based on the fluorescent enhancement and quenching with multiple analytes [149, 150]. Generally, the performance of the CDs in sensor applications is evaluated under two primary criteria: selectivity and sensitivity. The selectivity is determined by the

drop/increase in fluorescence in CDs towards the targeted analyte at a predefined concentration. If this is significantly different compared to other potentially interfering substances, the CDs have high selectivity. Typically, for good selectivity the fluorescence enhancement/quenching ratio of the targeted analyte over other compounds should be at least 5 times [151, 152]. The sensitivity is quantified by how well the fluorescence change to the analyte concentration. This is evaluated by the linear range and the limit of detection (LOD). Table 2-4 summarizes some of the sensing performance of CDs.

Table 2-4: Summary of CDs as a sensor and the corresponding performance

Group	Analyte	CD Precursor	QY%	LOD	Linear Range	Ref
Cation	Fe ³⁺	citric acid/ tris	52%	1.3 μ M	0-50 μ M	[153]
	Hg ²⁺	citric acid/ urea/ l-cysteine	25%	2 μ M	0-40 μ M	[46]
	Cu ²⁺	citric acid / mesoporous silica	7%	23 nM	0-10 μ M	[154]
	Cr ⁶⁺	citric acid / diethylenetriamine	88.6%	-	0.01-50 μ M	[155]
	Pb ²⁺	Glycerol/ ethanolamine	-	15 nM	0.1-6 μ M	[156]
	Ag ⁺	Dihydric alcohol	3.02%	0.32 μ M	0-90 μ M	[148]
Anions	PO ₄ ³⁻	citric acid/ aminoundecanoic acid		51 nM	0.4- 15 μ M	[157]
	ClO ⁻	Fish Scale	19.3%	50 nM	0.1-300 μ M	[158]
	S ²⁻	citric acid / ethylenediamine	-	0.78 μ M	0-25 μ M	[159]
	CN ⁻	citric acid / branched poly ethylenediamine	42.5%	0.65 μ M	2-200 μ M	[160]
Others	Glucose	citric acid / ethylenediamine	-	0.35 μ M	10-200 μ M	[161]
	Cysteine	Citric acid / Ammonia	35.4%	0.79 nM	0-50 μ M	[162]
	Alkaline phosphatase	Activated carbon /H ₂ SO ₄ /HNO ₃	2.2%	1.1 U/L	16.7-782.6 U/L	[163]
	Tetracycline	Citric acid / K ₂ HPO ₄	-	5.48 nM	0.02-14 μ M	[164]

2.4.2 Bioimaging

High biocompatibility and low toxicity has made CDs a competitive alternative for the commercial CdSe-ZnS based quantum dots in the bioimaging field [165]. Promising results of CDs have been studied both *in vitro* experiments involving cellular uptake and *in vivo* studies primarily based on mice models. Generally, *in vitro* studies are performed to determine bioimaging ability, distribution and cytotoxicity of the fluorescent probe with respect to the cells [166]. The first CD based imaging was done for Caco-2 cells [167] and thereon CDs have been extensively used to image wide variety of cells including HeLa cells [168, 169], HepG2 [170], NIH-3T3 fibroblast cells [171], LLC-PK1 [172], human lung cancer A549 cells [173], MCF-7 cells [174] and human neural stem cells [175]. Surface modification is an essential step in developing high fluorescent carbon dots with targeted cell uptake. For example, Zhai et al developed nitrogen doped CDs from citric acid and 1,2-ethylenediamine (EDA) which enhanced the PL properties significantly to provide high quality bright images of L929 cells (Figure 2-10a) [176]. Further, these cells are observed to be in the cell membrane and cytoplasmic area which coincide with most reports [166]. Apart from low toxicity, possibility of tuning CDs for PL emissions in the near infrared (NIR) region is critical for the successful application for *in vivo* imaging because of the body tissue transparency in the NIR region [59]. Figure 2-10b represents an *in vivo* image of a mouse injected with CDs subcutaneously at three different locations [177].

Figure 2-10: (a) Laser scanning confocal microscopy images of L929 cells without labeling as a negative control (left (a)) and EDA-CDs labeled L929 cells (left (b)) and (b) In vivo fluorescence images of a Cdots-M-injected mouse at different excitation wavelengths. Adopted from [176, 177]

It is observed the injected spots of CDs are clearly distinguishable (Red) from the autofluorescence of the tissue (green). Li et al used blue fluorescent CDs for *ex vivo* experiments on various organs of a mice and were able to successfully image heart, lung, liver, spleen, kidney, intestines and even the brain which indicate the CDs were able to cross the blood brain barrier [178]. Thus, CDs are a promising source of fluorescent probe for both cellular detection and *in vivo* imaging.

2.4.3 Photocatalyst

Photocatalysis can be considered a green method to catalyze reactions, generate energy and reduce pollutants. In general usage of CDs in these applications can be of two formations [179]. One is using pure CDs where functional groups and dopants are used to create additional energy bands for enhanced photocatalysis activity and the other is using CD based composites where existing photocatalysts are used together with CDs

for efficient charge separation [179-181]. Based on this formation, application of CDs in photocatalysis can be categorized into four main reaction areas. First as a photocatalyst for pollutant degradation. For instance, CD composites were used to degrade organic dyes like Rhodamine B [182] and Methylene Blue [183, 184]. In addition, CD/Cu₂O, CD/Fe₂O₃ and CD/ZnO composites were used to degrade ethyl paraoxon pesticide, gas-phase benzene and methanol respectively [185-187]. Second, for H₂ and O₂ evolution reactions by water splitting in which case CDs acts as photosensitizers that has a broader absorption in the visible area [188, 189]. Thirdly, in the CO₂ conversion reactions where CD coated electrodes in optical cells is photo irradiated to reduce CO₂ in to different products including CO, organic acids, methane or other hydrocarbons [179, 190, 191]. However, CD based systems for large scale CO₂ reductions models are yet to be investigated and should be a high focused area considering the positive impact on greenhouse gas emissions by CO₂ reduction. Finally, CDs have also been used for other photocatalytic chemical reactions including selective oxidation and acid catalysis [179]. For instance, high surface area, absorption capacity and/or surface functionality has governed these selective reactions including oxidation of benzyl alcohol and cyclohexane [192, 193], reduction of nitro-benzene derivatives [182] and catalysis of organic reactions [183]. Although the application of CDs in photocatalytic reaction has rendered favorable results, large scale production, commercial applications and recovery areas are yet to be investigated in future works.

2.4.4 Photovoltaic

Display of high optical absorption across the full visible spectrum, tunable bandgap and the functionality of CDs to act as an electron donor/acceptor or as a conducting medium for electron transfer has made CDs a promising candidate for number of photovoltaic

configurations. These include acting in the role of a dye sensitizer, dopant in the photoactive materials, electrolyte or a counter electrode [58, 194].

Dye sensitized solar cells (DSSC) is one of the most commonly used type of solar cell due to the low cost and ease of production [195]. Basic mechanism of a DSSC involves the absorption of the incident light by the dye to generate excited electrons which are then injected into the conduction band of the TiO_2 electrode [194, 195]. Wang et al synthesised a DSSC using nitrogen doped CDs as the dye medium [196]. As shown in Figure 2-11a, the doping of nitrogen creates additional energy bands between π of carbon and π^* of oxygen which are essential to absorb low energy photons in the visible range. Thus, it will generate more photoexcited electrons to transfer to the TiO_2 conduction band to result on higher current density. In addition to the current, CDs are rich in carboxyl groups which can chemisorb into the TiO_2 surface creating a covalent link and thereby forming an efficient passage for the electrons to transfer to the TiO_2 [194].

Another common configuration is Bulk heterojunction organic solar cell (BHJ- OSC) where the active layers comprises of donor and an acceptor. As shown in Figure 2-11b, once the donor gets excited the excitons get transported to the donor-acceptor interface and the separated electrons and holes are transported to the electrodes without recombination [197]. The CDs electron donating/acceptance characteristic is critical for a successful design of such devices [56]. CDs have also been used in other solar cell configurations. For instance, Briscoe et al used biomass derived CDs in the solid state DSSC, where the disadvantages associated with general DSSC (e.g. leakage of the liquid electrolyte, corrosion) can be mitigated by the use of a solid electrolyte material [198, 199]. Even with these developments, it should be noted that usage of CDs in solar

cells is still at a nascent stage and there are many areas that need to be improved before developing it to a viable prototype.

Figure 2-11: (a) A proposed model of photoinduced electron transition between NCDs and TiO_2 and (b) Steps involved in energy production in a BHJ-OSC cell.

Adopted from [196, 197].

2.4.5 Nanomedicine

Key criteria to use nanoparticles as carries in biomedical applications is to avoid blood vessel blockages since the particle size or the aggregates of the particles can be kept below $4\mu\text{m}$ which is the smallest diameter of the blood capillaries in human body [200]. In addition, excellent biocompatibility leading to low cytotoxic effects, high surface activity and enhanced cellular uptake has paved the way for CDs to be an efficient nanomaterial for theragnostic medicine including drug and gene delivery [62, 201]. The CDs surface is rich in oxygen/nitrogen functional groups (e.g. $-\text{NH}_2$, $-\text{OH}$, $-\text{COOH}$ etc) which provides a platform to carry therapeutic drugs via electrostatic interactions or covalent bonding [201]. For example, Kong et al developed carbon dots via

hydrothermal approach from citric acid ethylenediamine [201]. The CDs were electrostatically conjugated with Doxorubicin drug to investigate the cellular toxicity and pharmaceutical activity on human breast adenocarcinoma cell line (MCF-7). The surface charges in CDs enabled to have a high drug loading capacity and moreover, the positive surface charges allow endocytosis which increases the cellular uptake of the drug [201, 202]. In addition to the drug delivery, CDs have been used in gene therapy where CDs acts as vectors to effectively transfer therapeutic gene to unhealthy cells [203]. Yu and his group used microwave assisted method to produce CDs from hyaluronic acid with polyethylenimine (PEI) as the passivating agent [203]. Synthesised CDs showed lower cytotoxicity and higher transfection efficiency in HeLa cells compared to PEI. They identified the core shell structure of the CDs with high amino functionalized surface enhanced the DNA binding and transfection efficiency. Further, the high fluorescence of CDs permitted the cell imaging which allows to monitor the DNA transportation process. The application of CDs can be multifunctional and are not just limited to transporting drugs/genes [58]. For example, wang et al prepared a hybrid nanocomposite with polyethylene glycol, chitosan and glucose derived CDs which can enter the intercellular regions to light the tumor cells, detect pH changes, facilitate pH sensitive drug release and trigger drug release by external irradiation of NIR light [204]. These multifunctional capabilities increase the therapeutic efficiency and provide an advanced platform for CDs to be used in biomedical field.

2.4.6 Opto-Electronics

Tunable emission and electron donating and/or accepting behaviour and strong absorptions has led to the use of CDs in optoelectronic devices like light emitting diodes

(LEDs) [56]. CDs are a promising alternative for rare and expensive metal based semiconductors and large PL gap has provided the opportunity to make white LEDs which is known for its long working life, low power consumption, fast response time and energy saving sustainable applications [58]. Based on the excitation method, LEDs from CDs can be classified into two types namely photoluminescence (PL) based or electroluminescence (EL) based. The PL based LEDs are basically the fluorescent CD powders on a chip that get photoexcited by a UV/blue light followed by emission of light in the visible region [56, 58]. One of the major limitations in this set up is aggregation induced quenching (AIQ) attributed to the excessive resonance energy transfer or direct π - π interactions which reduce the QY significantly [205, 206]. To avoid this undesirable quenching, CDs have been embedded into a solid state matrix such as borax, polyvinyl alcohol (PVA), inorganic salts, silicone and starch [58, 205]. However, developing matrix based LEDs from CDs is time and energy consuming process and recently producing CDs with modified surfaces to control the interparticle distance has been studied. Liu and his group synthesised nitrogen doped CDs from PVA and ethylenediamine which emits yellow-green light under solid state and blue colour in solution [206]. The surface of the CD is decorated with PVA chains and amino groups and the formed aggregates did not quench since the graphitized cores cannot directly contact owing to the steric hindrance of the PVA chains.

The EL based LEDs basically convert electrical field/current into light by the use of an emission layer of CDs sandwiched between multilayer structure of hole/electron transport layers [58, 207]. Rogach et al synthesised similar multilayer device from a same size CD emissive layer that can emit multicolours including blue, cyan, magenta and white by tuning the multilayer properties and applied voltage [207]. Although progress of CD based LED devices is promising, developing high QY CDs in solid state

and optimizing multilayer properties for better charge transfers are still need be studied for a better comparison with well-developed heavy metal based LEDs.

2.5 Cellulosic biomass for CD production

As discussed in the introduction, the use of cellulosic biomass for the CD production has multiple advantages including access to an abundant renewable resource, low cost, high biocompatibility, facile synthetic techniques and low toxicity [1, 15, 16]. Thus, considerable attempts have been made to generate CDs from cellulosic biomass which have been tabulated in table 2-5.

Table 2-5: Comparison of CD properties derived from various cellulosic-biomass precursors

Biomass Precursor	Operational Condition	Pre/Post Chemical Treatment	MY	QY	Ref.
Pomelo Peels	HTC 200 °C / 3 hrs	-	-	6.90%	[5]
Eucalyptus kraft pulp	Oxidation with HNO ₃	-	-	1.20%	[39]
		Reflux with thionyl chloride	-	3.20%	[39]
Bagasse	HTC 220 °C / 1 hr	H ₂ SO ₄ + H ₃ PO ₄ + Fe ₂ (SO ₄) ₃	-	2.70%	[40]
Grape Peels	HTC 180 °C / 6 hrs	-	-	3.10%	[41]
Sheep Wool	Microwave 200 °C /1 hr	-	-	16.3%	[105]
Bagasse	HTC 180°C /3 hrs	Add NaOH	9.30%	12.30%	[130]
Orange Peels	HTC 180 °C / 12 hrs	H ₂ SO ₄ + NaOCl	12.3%	36%	[133]
Corn Stalks	HTC 160 °C/10 hrs	-	-	7.60 %	[208]
Sugarcane Molasses	HTC 250 °C /12 h	-	-	5.8%	[209]
Gynostemma	Calcined 400 °C /4 h	-	-	5.7%	[210]
Grass	HTC 180 °C / 3 hrs	-	-	5.1%	[211]
Miscanthus grass	Heating 180°C /4 hrs	-	-	4.71%	[212]
Bamboo leaves	HTC 200 °C / 6 hrs	-	-	7.1%	[213]

Several observations can be drawn from the results tabulated above. First, facile hydrothermal/ microwave/ conventional heating methods can be adopted to successfully produce fluorescent carbon dots which positively contribute to the sustainable and green synthesis of functional materials. Second, compared to conventional precursor materials like citric/ acrylic acids [214, 215], the quantum yields of cellulosic biomass derived CDs are relatively low. However, few studies have successfully managed to synthesis high fluorescent carbon dots through the use of nitrogen, sulfur and phosphorus incorporating chemical treatments [130, 133] which suggest further experiments have to be conducted to develop new synthetic routes or dopants for cellulosic biomass to yield CDs with a similar performance to conventional precursors. Third and most importantly, some cellulosic biomass has incorporated the naturally existing heteroatoms and/or functional groups to generate high fluorescent carbon dots. For example, pomelo peels and orange peels are rich sources of citric acids that have contributed to the higher quantum yield (QY) of their corresponding CDs [5, 133, 216] and sheep wool is a rich source of protein and constitute nitrogen (16-17%) and sulphur (3-4%) which lead to the enhancement of PL without any additional treatments [105, 217]. Moreover, Liu et al identified the high PL in CDs synthesised by bamboo leaves are primarily due to the large amounts of hydroxyl and carboxylic moieties present in the precursor [213]. Thus, it is evident that the functional groups/ heteroatoms present in the cellulosic biomass composition plays a vital role in the quality of the CDs and identifying these constituents is critical to explore the full potential of biomass and model future pathways for CD production.

2.6 Overview of durian waste

Durian (*Durio zibethinus*) is one of the most popular seasonal fruit in Southeast Asian countries with an annual production around 1.4 million tons [218]. Locally known as “king of fruits”, it belongs to the Bombacaceae family and Durio genus [219]. Durian, featured by its strong pungent odour was first commercially harvested in southeast countries from mid-20th century and since then the durian has been used as a directly consumed fruit as well as a flavouring agent in food processing industries (e.g. ice cream, tarts, jams and cakes) [33]. Currently, Thailand, Malaysia, Indonesia and Philippines are the largest producers which accounts to over 90% of the global durian production with China, Singapore and Taiwan being the key importers controlling over 65% of the total durian imports [33]. Despite the increasing demand for the fruit, one of the major hindrances for its use in commercial scale is the large quantity of unconsumable waste generated in the form of shell and seeds which accounts to a total of 70% of the fruit mass [33, 220].

Durian seed which adds up to 5- 20% of the fruit mass is a rich source of carbohydrate (~ 46%) and small amount of protein and gum [221, 222]. The high starch content and the chemical composition has led to extensive studies on the application of durian seeds in multidisciplinary fields. For example, durian seed starch has been used as a natural reinforcement filler for polymer material for improved thermal and biodegradable properties [222], a substitute for wheat flour or as a thickening agent in food industry [221, 223], replacement as a binding agent for wood charcoal briquettes [220], a feedstock for bioethanol production [224, 225] and as an adsorbent [226, 227].

More than 50% of the Durian is composed of the shell which is a combination of cellulose, hemicellulose and lignin along with minor levels of oxygen/ nitrogen

functional groups containing extractives [12]. Table 2-5 shows the proximate and ultimate analyses of the durian shell/peel conducted by previous studies.

Table 2-6: Proximate and ultimate analyses of the durian shell

Proximate analysis (g kg ⁻¹)				Ultimate analysis (g kg ⁻¹)					Ref
Moisture	Volatile matter	Fixed carbon	Ash	C	N	H	O	S	
55.3	695.9	223.6	25.2	603.1	30.6	84.7	280.6	1.0	[228]
45.4	698.2	214.2	42.2	428.6	1.8	57.1	512.5	-	[229]

Unlike the durian seed, the application of durian shell has been limited and mostly focused as a biomass to synthesis activated carbon. Durian shell waste activated char has been used as an adsorbent for water vapour [230], methylene blue [231], acid green [232], bisphenol [233], basic green [229] and cadmium ions [234]. However, these applications are rudimentary and lack the use of specific properties associated with durian shell. Nevertheless, there have been few studies where the high lignocellulosic nature of durian shell has been exploited to produce more novel products like bacterial cellulose [235], dietary fiber in functional foods [236] and cellulose-cement sheets for building insulating material with improved thermal, rheological, mechanical properties [237]. Moreover, there have been developments where the durian shell has been further processed to extract water soluble polysaccharide gel with importance in the pharmacological and food processing industries as a result of antibacterial, immunostimulant and cholesterol reduction properties [238, 239]. Also, durian shells have been used as a source to extract pectin [240, 241] and fermentable sugars [242]. Nevertheless, most of these value added products required extensive pretreatment and

purification steps and the use of high purity chemicals and thus lacks the environmental and commercial feasibility.

2.7 Summary and Research Gaps

According to the literature review several research gaps have been identified and summarized as follows;

- 1) Carbon dots are novel and unique structure in the functional carbon nanomaterials field and development of CDs from biomass is a promising sustainable pathway. Biomass naturally contains many minerals, oxygen/sulfur/nitrogen functional groups which have been predicted to affect the fluorescence. Thus, there is a demand to identify the effects of the composition of biomass to the overall performance of the CDs. Further, most biomass precursors use hydrothermal carbonisation or microwave digestion methods for CD generation. Although these are facile techniques there is a downside of controlling the size of the particles leading to multistep post separation treatments. Thus, improvements in size control should be investigated. Finally, models and mechanisms need to be developed with this information to better predict and identify novel carbon precursors and synthetic routes for CD development.
- 2) Cellulose is the primary constituent in biomass and considering the carbon rich nature of the source, usage of these biomass precursors can be viewed as an optimal progression for new carbon materials. However, low quantum yield is one of the major challenges that need to be addressed. Thus, novel synthetic routes with pre/post treatment techniques and targeted doping agents need to be investigated in future studies.

- 3) Due to the chemical, physical and optical characteristics, CDs have been used in multidisciplinary fields including sensing, imaging, photocatalyst, solar cells and nanomedicine. However, there is much to be improved through a more targeted approach. For example, sensing and bioimaging are the main application fields of biomass derived CDs. However, detail mechanisms of CDs interactions with different analytes/cells need to be developed for enhanced sensing performance. This understanding can optimize detection limits and reduce environmental interferences for more targeted performance. Further, majority of CDs applied as photocatalyst, solar cells, LEDs and nanomedicine are based on synthetic precursors. Thus, experiments with sustainable and less expensive materials need to be conducted and large scale synthesis with technical and economic feasibility should be evaluated.
- 4) Durian shell waste has imposed a significant challenge as a municipal solid waste and there have been only few attempts to convert it as a value added cellulose product or as a source for high value chemicals. However, these attempts involved complex extraction methods or the use of expensive chemicals which rendered it a challenging precursor for large scale production. Moreover, the lack of a detailed study of the constituent of the durian shell has prevented from identifying the full potential of the durian shell. Thus, it is important to identifying durian shell composition and moreover develop facile synthetic methods and products that can bring significant value for this underutilized resource.

Chapter 3 Production of carbon dots from DSW

Durian shell waste is a cellulose rich source and is used for the first time in a one-pot process without any modification agent to produce CDs. The presence of carboxylic acids, esters and amino compounds in durian shell was crucial to improving the CD surface and resulting in a mass yield of 13.9% and quantum yield of 6.2%. This was two times higher compared to that of CDs derived from pure cellulose precursors. The blue-green emitting CDs showed stability over a wide range of pH and chloride concentration and was resistant to photobleaching. Further, the CDs showed high selectivity towards Fe^{3+} by forming a non-fluorescent ground complex with the oxygen functional groups. Based on the linear relationship between normalized fluorescence intensity and concentration of Fe^{3+} ions, the synthesised CDs may be used as a fluorescent probe to detect Fe^{3+} over a concentration range of 0-20 μM with a detection limit of 128 nM. The method was successfully applied in sensing Fe^{3+} in actual water systems. Finally, selected nitrogen, sulfur and oxygen and phosphorus functional group containing dopants were used to investigate the effect to the QY of cellulose and DSW derived CDs.

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3.0 Introduction

Carbon dots (CDs) is an emerging type of nanomaterials that has attracted research interest due to its physicochemical properties such as tunable photoluminescence, high biocompatibility, easy functionalization, water solubility and low toxicity [4, 5, 39]. As discussed in the previous chapter, synthesis of CDs can be by either a “top-down” approach like laser ablation [167], electrochemical [243] and oxidation [89] or a “bottom-up” approach like hydrothermal [244, 245], microwave [246] and pyrolysis [247]. However, hydrothermal carbonisation is selected as the synthetic method to produce CDs from biomass due to the cost effective, nontoxic and nature [8].

Durian, dubbed ‘the king of fruits’, is a popular tropical fruit with an The average fruit weighs 1-3 kg out of which two thirds are the shell [34, 37]. Durian shell waste (DSW) comprises mainly cellulose, hemicellulose and lignin and these account for 90% while the remaining consists of extractives such as carboxylic acids, phenolic compounds, and esters. This 10% enhances the oxygenated functional groups in DSW [248]. According to the literature, the high cellulose containing carbon materials have yielded low photoluminescence (PL). PL is one of the key characteristics in CDs which determines performance and is dependent on several factors, including the quantum confinement effect governed by particle sizes, surface traps, edge states and heteroatoms [42]. Thus, the purpose of this study is to identify whether naturally present functional groups and heteroatoms in DSW will have a significant impact on the luminescent characteristics of CDs and their sensing applications.

Iron is one of the most essential minerals in biological systems. However, excess intake of iron has been linked with diseases of aging like Alzheimer’s and other neurogenerative diseases [249]. Further, the presence of iron in water causes odours

and enhances the growth of iron bacteria which produces slime that can stain and block the plumbing [250]. Thus, selective and sensitive determination of iron is important. The current methods for determination of metal ions in water involve relatively expensive atomic absorption spectroscopy (AAS), inductive coupled plasmon mass spectrometry (ICP-MS), or atomic fluorescence spectroscopy (AFS) which require time, skill, and controlled laboratory environments [45]. With these limitations, there is an increasing interest in fluorescent probes as an analytical tool to detect iron due to their sensitivity, selectivity and rapidity [251]. In recent years, several works have been reported in association with Fe^{3+} detection but most of these works include one or more mixes of sulfur, nitrogen and phosphorous doping [252-255]. Thus, there is interest to identify biomass compounds with naturally existing doping molecules that can improve the CD surface structure, and so not only enhancing the photoluminescence but also exhibit high selectivity, biocompatibility and sensitivity towards Fe^{3+} .

In this study, a simple one-step method is developed to synthesis fluorescent carbon dots from DSW. The operational conditions were optimized for maximum quantum yield. Secondly, the produced CDs were compared and characterized by its physical, chemical and optical properties. Thirdly, the CDs were used in the detection of Fe^{3+} ions to develop a good linear relationship ($R^2 = 0.997$) between fluorescent quenching and the concentration of Fe^{3+} . This relationship was validated with three real water systems and the method of fluorescent quenching was explored to understand the detection mechanism. Finally, extractives present in the DSW is analysed in detail to further identify the functional groups in DSW. These functional groups were further analysed by their effect to the PL enhancement of DSW and pure cellulose based CDs.

3.1 Materials and Methods

3.1.1 Chemicals

Quinine sulfate, NaClO_2 and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were purchased from Alfa Aesar, US. CH_3COOH , $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, NaOH and NaCl were obtained from Merck Pte. Ltd, US. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ were purchased from Sinopharm Chemical Reagent Co. Ltd, China. Dichloromethane, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, ZnCl_2 , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were obtained from Sigma-Aldrich Co. LLC, US. All the chemicals were of analytical grade and used as received.

3.1.2 Sample Preparation and Extraction

DSW was obtained from a local market and processed in the laboratory (Figure 3-1). Washed and dried pieces of DSW were grounded with a ball mill (RETSCH PM 100) and sieved with a 60-80 wire mesh before storing at 4°C until required.

The extraction of cellulose and hollocellulose from the durian shell was done according to Penjumras et al. with minor modification [256]. First, 20g of dried DSW powder is added with 640 ml of DI water and the mix was kept at 70°C water bath. Then, 4ml of glacial acetic acid and 8g of NaClO_2 were added every hour for 5 hrs. Once the mixture cooled down, the white holocellulose was filtered and washed repeatedly with DI water. To obtain cellulose, hollocellulose was added with 80ml of 17.5% NaOH solution and subsequently 40ml of the NaOH solution was added three times at 5 min interval while mixing thoroughly. After the mixture was kept for additional 30 mins, 240 ml DI water was added and kept for another 60 mins before filtering. Finally, the filtered cellulose was rinsed with 800ml of 8.3% NaOH solution and the resulting mixture was

neutralized with 10% acetic acid before the final filtration and rinsing. The filtered cellulose product was stored at 4 °C after overnight drying at 80 °C.

The extraction of extractives was done using the Soxhlet apparatus with three solvent: DI water, ethanol and dichloromethane. The extraction process was based on the laboratory analytical procedure for the determination of extractive in biomass [257] and the resulting extractives were analyzed in an Agilent Liquid Chromatography Quadrupole Time-of-Flight Mass Spectrometer with a Zorbax SB-C18, 2.1x100mm, 1.8 mm column. The minerals present in the DSW are investigated by mixing 10.0mg of powdered DSW with 8 ml of 70% HNO_3 and 2 ml of 35% H_2O_2 in a Teflon lined reactor and then subjecting the solution to microwave digestion at 180°C for 20 mins. Once the solution was cooled down, it was filtered by 0.2 mm syringe filter and mineral analysis was done through inductively coupled plasma optical emission spectrometry.

Figure 3-1: Schematic illustration of the preparation of DSW and extraction of cellulose and extractives from DSW

3.1.3 Synthesis of CDs

Powdered DSW (1g) was mixed with 25ml of deionized (DI) water and sealed into a 45ml Teflon-lined stainless steel autoclave and heated at 210 °C for 12 h. The heating rate was maintained at 5°C/min. The formation of CDs was indicated by the dark brown solution formed by the reaction. After the mixture was naturally cooled to room temperature, the larger particles were filtered with a 0.45 µm filter followed by 0.22 µm (Whatman) filter papers. The solution was then mixed thoroughly with 10 ml of dichloromethane to remove any unreacted organic moieties and centrifuged at 10000 rpm for 15 min to separate the CD solution. The resulting CD solution was stored at 4°C until further characterization.

3.1.4 Characterization of CDs

Characterisation of the surface of CDs was performed with Fourier transform infrared spectroscopy on a Bruker Tensor 27 FTIR spectrophotometer. JEOL JSM 7200F field emission scanning electron microscopy (FE-SEM) was used for elemental mapping of CDs. HORIBA XploRAPLUS Raman Microscope was used to perform the Raman pattern. X-ray photoelectron spectroscopy measurements were performed on a Kratos Analytical AXIS Supra photoelectron spectrometer. X-ray Diffraction was obtained with the Bruker D8 Advance X-ray Powder Diffractometer. Morphology of CDs was investigated with a JEOL 2010 HR transmission electron microscope. Agilent Cary Eclipse Fluorescence Spectrophotometer was used for all fluorescence spectral measurements. Ultraviolet-Visible absorption spectra were obtained with an Agilent Varian Cary 50 UV/Vis Spectrophotometer. Time resolved fluorescence spectroscopy was performed on a Horiba fluorolog-3 spectrofluorometer equipped with a 360nm nanoLED. Fluorescence decay data was analyzed by DAS-6 Horiba software.

Thermogravimetric analysis was done with the NETZSCH STA 449 F3 Jupiter Simultaneous Thermal Analyzer.

3.1.5 Quantum Yield (QY) Measurement

The fluorescence quantum yield of NCDs was determined using quinine sulfate (QY is 54% in 0.5 M H₂SO₄ solution) as a standard sample at 366 nm excitation wavelength and calculated with the following equation [258]

$$QY_{CD} = QY_{st} \left(\frac{I_{NCD}}{I_{st}} \right) \left(\frac{A_{st}}{A_{CD}} \right) \left(\frac{\eta_{CD}}{\eta_{st}} \right)^2$$

where subscripts “NCD” and “st” stands for NCDs and reference standard respectively. “I” refers to the integrated Photoluminescence (PL) intensity, “A” refers the absorbance measured at the excited wavelength and “η” refers to the refractive index. To minimize re-absorption effects in the 10 mm fluorescence cuvette, absorbencies were kept under 0.1.

3.1.6 Fe³⁺ Detection

To assess selectivity, Mg²⁺, Ca²⁺, Zn²⁺, Fe²⁺, Fe³⁺, Cr³⁺, Co²⁺, Na⁺, Pb²⁺, Cu²⁺, La³⁺ and Ni²⁺ metal ions were evaluated with the CDs. In a typical detection assay, metal ion concentration was 200 μM while the CD concentration was 125 μg/ml. The sensitivity to Fe³⁺ ions was determined with a series of Fe³⁺ concentrations ranging from 0 - 150 μM. After each addition of Fe³⁺, the solution was mixed thoroughly. The PL spectrum was recorded at an excitation wavelength of 360 nm after 5 min at room temperature. All measurements were performed in triplicates with DI water at room temperature. The practical application of CD/Fe³⁺ system was evaluated by challenging it with three different water samples (lake water, seawater, and tap water). Lake water was obtained

from Jurong Lake and seawater was obtained from the intake of Tuas desalination plant. After filtering through a 0.22 μm syringe filter, 2 ml of each water sample was spiked with a known concentration of Fe^{3+} and a CD concentration of 125 $\mu\text{g/ml}$.

3.2 Results and Discussion

3.2.1 Extraction of Cellulose from DSW

Thermal decomposition of the DSW and extracted cellulose was shown in Figure 3-2a. Two distinct regions of thermal decomposition can be observed for cellulose which is consistent with literature [259]. First region is located at the beginning where volatilization and vaporization of cellulose occurred and from 100-245 $^{\circ}\text{C}$, the mass remain constant. However, rapid decomposition occurred from 245- 390 $^{\circ}\text{C}$ which was mainly due to the dehydration and decomposition of cellulose. Decomposition of DSW occurred from 200 $^{\circ}\text{C}$ onwards which was because of hemicellulose decomposition [37]. Compared to cellulose, DSW has a higher retention of mass at 350 $^{\circ}\text{C}$ which was mainly due to the lignin which generally decompose from 160 -900 $^{\circ}\text{C}$ [260].

Figure 3-2: (a) Thermogravimetric Analysis and (b) FTIR spectra of DSW and cellulose

From the FTIR analysis of the cellulose and DSW, several distinguishable peaks can be observed (Figure 3-2b). The peak around 3300 cm^{-1} corresponds to the -OH stretching group and the high intensity peak for cellulose suggest the extracted cellulose contain more -OH groups [256]. Further, the absorption DSW shows an absorption peak around 1237 cm^{-1} which indicate the -CO groups of acetyl present in lignin but this is absent from cellulose indicating the lignin has been removed during the extraction process [261]. The strong peaks around 1050 cm^{-1} and at 892 cm^{-1} is due to the glycosidic -C-O-C and -CH vibrations unique to cellulose [262, 263]. Based on these analyses it can be concluded that cellulose has been successfully extracted without changing the molecular structure from DSW.

Biomass generally contains minerals which can be macronutrients like potassium, magnesium, calcium and phosphorus and also micronutrients like boron, iron, zinc and copper [264]. Thus, mineral content in DSW is investigated and the overall detectable mineral content by ICP-OES is less than 0.2% of the dry mass. Elemental analysis of the minerals in DSW showed the presence of potassium, calcium, magnesium and zinc with a dry weight percentage of 0.11, 0.05, 0.03 and 0.005 respectively.

3.2.2 Yield comparison of DSW-CDs and Cellulose-CDs

The operational condition of $210\text{ }^{\circ}\text{C}$ with a residence time of 12 hrs was selected based on the 2×2 temperature-residence time matrix. Mass yield (MY) (Figure 3-3a) and QY (Figure 3-3b) were measured at each temperature ($180\text{ }^{\circ}\text{C}$, $210\text{ }^{\circ}\text{C}$) and residence time (6 hrs, 12 hrs) to select the operational condition in which maximum photoluminescence was given. MY was calculated by the ratio of dry CD mass obtained following freeze drying the solution to the mass of DSW used. MY was calculated to be 13.9%, and 7.3% while QY was 6.2% and 3.1% for CDs based on DSW and

cellulose, respectively. The increase of MY with temperature is attributed to the higher hydrothermal degradation of cellulose above 200 °C which led to more nucleation and growth of CDs [265]. Moreover, higher dissolution of precursors increased the presence the intermediary products like acid groups, phenols and aldehydes that can improve the surface state of CDs to enhance the QY [74]. However, when the residence time is increased the reaction conditions get more severe leading carbon particles to grow larger than the intended 2-20 nm. These large particles get separated in the filtration and dialysis steps and thereby reducing the mass yield of CDs.

Figure 3-3: (a) Mass Yield and (b) Quantum Yield of DSW and cellulose CDs with HTC temperature and residence time

3.2.3 Extractive Analysis of DSW

Extractives analysis of durian shell identified 29 different oxygen and nitrogen groups including 10 carboxylic acids, 4 amino acids, 4 phenolic/quinone groups and 7 other amine/nitrogen containing compounds (Table 3-1). Carboxylic acids and alcohols can provide colloidal stability, control particle morphology and particle size distribution while preventing uncontrolled growth and agglomeration in quantum dot synthesis

[266] which increased the mass yield of nanoparticles [267]. Additionally, oxygen-rich functional groups including, -COOH, -HC=O and -OH are expected to provide further improvements such as versatile anchoring points for the dopants [268]. These groups also create additional surface defect sites on the CDs which will trap the excitation energy and lead to fluorescence emission by radiative recombination of the excitons trapped at the defects [269]. Furthermore, heteroatoms including nitrogen could create emissive trap states for photoexcited electrons, which modify the band gap energy and changes the optoelectronic properties to enhance the QY of DSW based CDs over cellulose precursors [44, 270]. Thus, the improvements in yields are attributable to the presence of surface functional groups provided by the extractives present in DSW.

Table 3-1: Extractive compounds identified in durian shells

Group	Compound	Molecular Formula	Score %*
Carboxylic Acid	Oleic Acid	C18H34O2	96.70
	2,3-dihydroxy-3-methylpentanoic acid	C6H12O4	99.82
	Methylmalonic acid	C4H6O4	99.79
	5-dehydro-4-deoxy-D-glucaric acid	C6H8O7	97.75
	2-Isopropylmalic acid	C7H12O5	96.32
	Maleic acid	C4H4O4	87.69
	Oxalosuccinic acid	C6H6O7	85.19
	2-Methylcitric acid	C7H10O7	82.65
	Acinospesigenin A	C32H50O6	80.67
	D-erythro-3-methylmalic acid	C5H8O5	99.84
Ester	Rhamnocitrin 3-glucoside-4'-(2"-dihydrophaseoylglucoside)	C43H52O20	85.64
	Malate	C4H6O5	94.07
	methyl 2-[methyl(prop-2-enoyl) amino] acetate	C7H11NO3	80.59
Phenols/Quinones/Alcohols	Lutein	C40H56O2	81.74
	L-gulono-1,4-lactone	C6H10O6	86.64
	menthyl beta-D-glucoside	C16H30O6	96.74
	Arbutin	C12H16O7	80.41
Amino Acid	2,3-Dihydroxybenzoylserine	C10H11NO6	97.38
	3,4-dihydroxy-L-phenylalanine	C9H11NO4	86.74
	Valinopine	C10H17NO6	80.53
	3-Amino-2,3-dihydrobenzoic acid	C7H9NO2	86.52

	1-Aminocyclohexanecarboxylic acid	C7H13NO2	82.68
Nitrogen Compounds	Desmethylniprenzepine	C18H19N5O2	82.55
	Debromohymenialdisine	C11H11N5O2	84.12
	Nifuradene	C8H8N4O4	83.61
	Bellendine	C12H15NO2	81.11
	2,4-Dihydroxypteridine	C6H4N4O2	94.97
	8-Cyclopentyltheophylline	C12H16N4O2	94.76
	3-Methyl-1-(5-oxohexyl)-7H-purine-2,6-dione	C12H16N4O3	92.48

*Score was given based on the similarity with METLIN database

3.2.4 CDs Characterization

Figure 3-4 shows the surface functionality of the DSW and corresponding CDs when examined with the ATR-FTIR. The CDs had functional groups similar to the DSW and the broad absorption peak at 3310 cm^{-1} corresponded to the phenolic-OH and N-H stretching vibrations [120]. The weak absorption peak at 2950 cm^{-1} was assigned to the C-H stretching vibrations while the peak at 2156 cm^{-1} is due to $\text{-C}\equiv\text{N}$ bond in aromatic cyano compounds [133, 271]. The absorption band at 1730 cm^{-1} in the DSW corresponds to the -C=O stretching of the aldehyde group [272] while in CDs this peak is observed to be at 1700 cm^{-1} . This shift in the -C=O peak corresponded with the stretching of conjugated aldehyde groups [272, 273]. During HTC, fractionation of biomass and structural aromatization steps causes the aldehydes to form these conjugations. Furthermore, the broad peak at 1604 cm^{-1} is the vibrational peak for the aromatic $\text{C}=\text{C}$ bending [120]. The peak at 1350 cm^{-1} was due to the stretching vibration of C-N [130]. The stretching vibration bands of C-O at 1050 cm^{-1} established the presence of carboxylic groups on the CD surface [127]. The glycosidic linkage from cellulose present in DSW caused a significant peak at 1050 cm^{-1} and this has reduced significantly after the destruction of cellulose structure during the hydrothermal process [39, 263].

Figure 3-4: (a) FTIR Spectra of DSW and synthesized CDs

The Raman spectroscopy analysis was conducted with excitation light of 532 nm in confocal mode and under 50x magnification (Figure 3-5a). It revealed two vibrational peaks, at 1365 and 1590 cm^{-1} , and these corresponded to the disordered (D) graphitic band and graphitic (G) band of sp^2 carbon atoms respectively [125].

Figure 3-5: (a) Raman Spectra and (b) XRD Spectra of CDs

The peak intensity ratio (I_D/I_G) correlated with D and G peaks was calculated to be 0.76 based on the peak intensity count. The graphitic structures were associated with sp^2 sites while the surface defects were mainly caused by the presence of oxygenated groups (C-O, C=O, O-C=O) [8]. XRD patterns were used to identify the degree of crystallinity of the synthesised CDs. As shown in Figure 3-5b, an intense broad diffraction peak around 22° was indexed to the (002) carbon lattice spacing and the peak at 16° indicated the presence of disordered carbon [246].

Figure 3-6: (a) TEM and the HRTEM (inset) images of the CDs and (b) Particle size distribution histogram of CDs as determined by TEM and (c) Elemental mapping of CDs showing carbon (purple), oxygen (green) and nitrogen (yellow)

Morphology of the CD particles was observed with TEM and the results shown in Figure 3-6a indicated the CDs were quasi-spherical and well dispersed. The HRTEM image (Figure 3-6a (Inset)) showed a lattice spacing of 0.38 nm which confirmed the crystalline features of the CDs and this was in agreement with the XRD results [274]. The particles ranged from 1-6 nm with average particle diameter at 3.2 nm (Figure 3-6b). Further, the EDS elemental mapping distribution of carbon, oxygen and nitrogen (Figure 3-6c) indicated the elements were evenly distributed on the CD surface.

Figure 3-7: (a) XPS spectrum of the CDs, (b), (c), and (d) High-resolution C1s, O1s, and N1s XPS spectra of the CDs

XPS results indicated the various functional groups present on CDs had an elemental composition of 78.94%, 20.29% and 0.77% corresponding to C, O and N elements (Figure 3-7a) respectively. The high resolution C1S spectrum showed three peaks (Figure 3-7b) with binding energies at 284.5, 286.4 and 288.3 eV. This corresponded to the C-C/C=C, C-O, and C=O bonds respectively [20, 275]. The O1s spectrum (Figure 3-7c) with two peaks at 531.3 and 533.5 eV, was due to C-O and C-OH/C-O-C groups, respectively [120]. The N1s spectrum (Figure 3-7d) showed two peaks at 399.7 and 400.1 eV, which were attributed to the C-N and N-H bonds [120]. XPS confirmed that the synthesised CDs' surface had carboxyl (-C=O), hydroxyl (-C-OH) and amine groups (-N-H) groups.

3.2.5 Optical Properties

The UV/vis absorption spectrum (Figure 3-8a) of CDs exhibited a significant broad peak at 280 nm and this was attributed to π - π^* aromatic sp² hybridisation [276]. Figure 3-8a inset shows that the CDs emitted a blue-green colour under a 365 nm UV lamp.

As shown in Figure 3-8b, a multi-emission fluorescence spectrum dependent on the excitation wavelength was observed and this was attributed to the synthesised CDs' various particle sizes as well as the creation of trap states by the functional groups on the surface [43, 277]. Once the excitation wavelength was increased from 340 to 460 nm, the maximum fluorescence emitted was red shifted from 432 to 505 nm. In addition, the strongest fluorescence emission was observed at 436 nm at the excitation wavelength of 360 nm which corresponded with the blue emission while a secondary peak could be observed at around 500 nm which correlated with green emission [73, 278]. The blue emission was due to the nitrogen doping of the graphitic structure [278]

and the green emission was mainly due to aldehyde (-HC=O) and carboxyl (-COOH) groups which enhanced the green fluorescence emission centers [279, 280].

Figure 3-8: The optical properties of the DSW-derived CDs. (a) UV/Vis absorption spectrum with maximum emission and excitation spectra and photograph of CDs under 365 nm UV light (inset) and (b) PL emission spectra of CDs at different excitation wavelengths from 340 to 460 nm

The overall results demonstrated DSW derived CDs possessed positive fluorescent properties. However, if the CDs are to be used under field conditions, the stability of PL intensity then would be an important aspect in the CD's deployment. To investigate this further, the PL intensity was measured against varying pH and ionic strength. The maximum PL intensity was measured at pH 6 while the lowest was at pH 3 and 11 (Figure 3-9a). However, the relative standard deviation (RSD) of the change in intensity was only 3.4% indicating the CDs can be used over a broad range pHs without significant change in intensity level. The fluorescent intensity change with ionic strength was measured following exposure to various concentrations of NaCl solutions

(Figure 3-9b). Even at a high salt concentration of around 200 mM, PL intensity was similar to the DI water (blank) solution. Generally, the fluorescence of CDs is governed by the size (quantum confinement effect), surface functional groups (surface state) and the presence of fluorescent molecules (molecular state) attached to the surface of CDs. However, if the ions do not interfere with these primary mechanisms the fluorescent intensity will remain consistent under varying ionic strengths in the environment. The stability of CDs at higher salt concentration indicated the CDs possessed high colloidal stability against particle-particle attraction forces [281].

Figure 3-9: (a) Effect of pH, (b) Effect of chloride concentration on PL intensity at 360nm excitation, (c) effect of Temperature and (d) Photostability of CDs under continuous UV irradiation

In contrast to the stability of fluorescence under pH and ionic content, the CDs PL intensity was slightly sensitive to the variations in the temperature (Figure 3-9c). The diminishing fluorescence with increasing temperature is credited to the activation of non-radiative thermal trappings [282]. The PL intensity of the CDs subjected to continuous UV irradiation for 120 mins (Figure 3-9d) showed CDs fluorescence reduced by only 10% and 14% after 60 mins and 120 mins of exposure. Traditional fluorescent dyes like Rhodamine 6G would have decayed by almost 45% of its original intensity after 120 min of continuous exposure. When compared with the latter, the synthesised CDs is more resistant to photobleaching [130]. Thus, the synthesised CDs have a good potential for sensor applications in water bodies with various salt concentrations and pH levels.

3.2.6 Selectivity and sensitivity in the Fe^{3+} detection

To explore the interference of Fe^{3+} to CDs fluorescence intensity several experiments were conducted. First, the selectivity of CDs towards 12 common metal ions - i.e. Mg^{2+} , Ca^{2+} , Co^{2+} , Fe^{3+} , Cr^{3+} , Pb^{2+} , Fe^{2+} , Ni^{2+} , Na^{+} , Zn^{2+} , Cu^{2+} and La^{3+} at a concentration of 200 μM each were tested with 12 $\mu\text{g}/\text{ml}$ CD solution. Figure 3-10 shows Fe^{3+} quenched 80% of the initial fluorescence intensity of CDs and showed high selectivity towards Fe^{3+} compared to other metals.

The fluorescence quenching by Fe^{3+} was explored further by measuring the decrease in PL intensity by continuous addition of known concentrations of Fe^{3+} from 0 to 150 μM (Figure 3-11a). As shown in Figure 3-11b, the quenching efficiency I_0/I displayed a good linear relationship with Fe^{3+} concentration with a correlation coefficient, R^2 , of 0.997 in a range of 0 -20 μM , where I_0 and I presented the fluorescence intensity in the absence and presence of the quencher, Fe^{3+} . The limit of detection (LOD) was

calculated to be 128 nM, based on $3\delta/m$, where δ is the standard deviation of the blank signal and m is the slope of the linear relationship.

Figure 3-10: Normalized PL intensity of C-dots dispersion with solutions containing different metal ions

Figure 3-11: (a) PL emission spectra of the CDs in the presence of various concentrations of Fe^{3+} and (b) Stern-Volmer plot as a function of Fe^{3+} concentration

The LOD calculated was significantly lower than the maximum allowable limit (5.375 μM) of Fe^{3+} in drinking water set by U.S environmental protection agency [254]. Table 3-2 compares the performance of Fe^{3+} sensing parameters including the linear detection range and LODs with recently published work. The results are either better or comparable and it should be noted the current results were obtained without using any doping agent or involving complex synthesis/modification processes.

Table 3-2: Comparison of different CDs used for Fe^{3+} detection

Precursor with Doping Agent	Linear Range (μM)	LOD (nM)	Ref.
Wheat Straw	0-250	1950	[244]
Rice Straw with AMIM-Cl doping	0-9	200	[283]
Radish	0.02-40	130	[284]
Phyllanthus acidus fruit with NH_3 doping	2-25	900	[285]
Mangosteen pulp	0-180	52	[276]
Goose Feathers	2-7	196	[106]
Cellulose fibers with H_2SO_4 doping	25-250	960	[286]
p-aminosalicylic acid with ethyleneglycol dimethacrylate	0.05-10	13.7	[253]
Copper nanoclusters with glutathione	1-100	300	[287]
Adenosine 5'-triphosphate	1-150	333	[254]
Durian shell waste	0-20	128	This work

3.2.7 Mechanism of Fe^{3+} detection

The fluorescence quenching can occur either as a combination of static quenching with a non-fluorescent ground state complex formation or by dynamic quenching where a transfer of energy or electrons occurs [288]. Further investigations were done to identify which mechanism was associated with Fe^{3+} quenching. Figure 3-12a displays the fluorescence lifetime spectroscopy results. The photoluminescence decay curves were fitted to a double-exponential function in the form of $A+B1 \exp(-t/\tau1) + B2 \exp(-t/\tau2)$ and the average decay time was calculated to be 3.04 ns ($\chi^2= 0.76$) and 3.07 ns ($\chi^2=$

0.76) with the quencher Fe^{3+} absent and present. This nearly identical values confirmed the PL quenching of CDs was caused by static quenching. Further, the detail parameters of the exponential functional is listed in Table 3-3 and the percentage contribution displayed alongside the τ values represent the relative amplitude. It is the ratio of photons coming from the different decays represented by $B_i\tau_i/\sum B_i\tau_i$. The average τ is calculated from the ratio of $\sum B_i\tau_i^2/\sum B_i\tau_i$.

Figure 3-12: Time-resolved fluorescence spectroscopy of CDs in the presence and absence of quencher

Table 3-3: Multi-exponential fitting of the TCSPC data of CDs in the absence and presence of Fe^{3+}

Parameter	τ_1 (ns)	τ_2 (ns)	Average τ (ns)	A	B1 (ns)	B2 (ns)
CD	1.55 (72.69%)	7.02 (27.31%)	3.04	0.235	1.553	7.021
CD + Fe^{3+}	1.55 (71.85%)	6.98 (28.15%)	3.07	0.292	1.556	6.981

To further elucidate the mechanism, the Stern-Volmer equation:

$$F_0/F = 1 + K_{sv}[Q]$$

where F_0 and F are the fluorescence intensity in the absence and presence of quencher Fe^{3+} , K_{sv} is the Stern-Volmer constant calculated to be $1.4 \times 10^4 \text{ M}^{-1}$ and $[\text{Q}]$ is the Fe^{3+} concentration was employed. The large magnitude of K_{sv} and the constant lifetime value further supported the argument the quenching was caused by the formation of a non-fluorescent ground complex between functional groups and the quencher Fe^{3+} [253, 289].

Figure 3-13: UV-vis absorption spectra of (a) CDs and CD-quencher complex and (b) CDs in the presence of non-quenching metal ions

Possible formation of ground state complex can be further investigated through the absorption spectra of CD-quencher complex. Figure 3-13a shows that addition of Fe^{3+} to the CD solution created a peak at 357 nm in addition to the CDs absorption peak at

280 nm. This contrasted with other metal ions where the peaks were consistent with the pure CD absorbance (Figure 3-13b). It was evident that in the presence of Fe^{3+} , -OH and -COOH groups on the surface of the CDs formed a non-fluorescent stable Fe^{3+} complex chelate causing non-radiative electron transfer of the excited electrons on CD to the Fe^{3+} [121, 290].

3.2.8 Application on real water systems

Water samples from three real sources were used in order to investigate Fe^{3+} detection by the synthesised CDs. The initial condition including total organic content (TOC), total nitrogen (TN) content and metal concentration measured by ICP-OES of the water samples are given in Table 3-4. Once the samples were spiked with known concentrations of Fe^{3+} , PL intensity was measured to calculate the recovery percentage and relative standard deviation (RSD). The results are shown in Table 3-5.

Table 3-4: Initial conditions of the actual water samples

Parameter	Unit	Lake Water	Sea Water	Tap Water
pH		7.61	7.81	7.02
Total Organic Carbon (TOC)	ppm	7.50	6.88	0.31
Inorganic Carbon (IC)	ppm	10.64	19.01	12.05
Total Nitrogen (TN)	ppm	1.14	0.26	0.43
Mg	ppm	1.680	1255	1.070
Cr	ppm	0.000	0.000	0.000
Cu	ppm	0.086	0.200	0.431
Fe	ppm	0.146	0.015	0.007
Co	ppm	0.003	0.100	0.005
Mn	ppm	0.062	0.050	0.003

The PL intensity of the water samples declined with increasing Fe^{3+} concentration and the recovery had been from 98.94%-108.61% while the RSD variation was from 1.09%-

4.11%. This supported the argument durian shell CDs has the potential to be used for Fe^{3+} detection in real water systems.

Table 3-5: Detection of Fe^{3+} in actual water samples (n=3)

Sample	Spiked Concentration (μM)	Measured Concentration (μM)	Recovery %	RSD %
Lake Water	4.00	3.96	98.94	3.95
	10.00	10.74	107.45	1.93
	20.00	21.72	108.61	4.11
Sea Water	4.00	3.98	99.42	1.39
	10.00	10.38	103.79	1.09
	20.00	20.66	103.30	2.19
Tap Water	4.00	4.08	102.01	2.39
	10.00	10.16	101.63	2.51
	20.00	20.31	101.53	2.59

3.2.9 Effects of functional groups on DSW and cellulose CDs

Extraction analysis of DSW identified carboxylic acids, amino acids and other nitrogen/oxygen containing functional groups including alcohols esters and amine. Carboxyl and amine groups are the commonly used surface functionalization groups for enhanced fluorescence in CDs since these functional groups introduce new energy levels between HOMO and LUMO energy levels [139]. However, interaction of the functional groups on the CD surface is varying and depended on the precursor composition and the synthetic route. Thus, for a better comparison how each of these common functional group effects with cellulose precursors, selected functional group containing doping agents were used and the QY of the resulting CDs were analysed (Figure 3-14). Terephthalic acid, 5-aminoisophthalic acid and histidine were used as dopants to represent carboxylic acid, amino carboxylic acid and amino acid respectively. Further, sodium sulfite, sulfuric and phosphoric acids were also used for

a better comparison. All doping agents were kept at a concentration of 0.4 mM and CDs were synthesised by the method explained in section 2.3.

Figure 3-14: QY of CDs produced from cellulose and DSW in the presence of selected functional groups

Except for carboxylic acids, similar pattern of fluorescence enhancement or reduction were observed for both DSW and cellulose derived CDs while the nitrogen doped agents gave the highest yield. Carboxylic acids on the CD surface can serve as electron withdrawing groups which lead to a reduction in the surface electron cloud [291, 292]. Consequently, this leads to non-radiative electron hole recombination to yield lower fluorescence. However, amine groups which are naturally present in DSW reduce this effect of surface carboxylic groups by converting them to amides and subsequently reducing the non-recombination effects [293]. Electron donating groups like amines increase the electron density which facilitates higher electron hole recombinations [291, 294]. Thus, it is suggested that amino groups in DSW facilitated the higher QY with carboxylic acids compared to cellulose. The significant QY difference attributed to the sulfates and sulfites could be due to the solvent effects and oxidation. Sulphates have

higher oxidation capability compared to sulfites and thus can oxidize the CD surface which can reduce the QY [73]. Further, the lone pairs contributed by the sulfites change the solvent properties that have reported to increase the fluorescence of CDs [295]. The phosphates addition has reduced the QY of CDs compared to the undoped CDs, and similar results have been reported by phosphorus doped *Miscanthus* grass derived carbon dots indicating the effects of phosphorus may not be effective to the fluorescence yield as nitrogen [212]. It should be noted that fluorescent mechanism of CDs is a complex process which is a resultant of multiple emission modes and thus requires a comprehensive future studies to identify the completed effects of dopants on the fluorescence of CDs.

3.3 Conclusion

A facile, one-pot hydrothermal carbonisation process was adopted to synthesise fluorescent CDs from DSW without any doping agents. Presence of carboxylic acids, esters, phenol, amino and quinone compounds in durian shell waste, enhanced the photoluminescence by enriching the CD surface with oxygen and nitrogen functional groups. The CDs showed good fluorescent properties and were stable over a wide range of pHs and chloride concentrations and were resistant to photobleaching which improved the CDs' usability under various environmental conditions. Thus, surface functional groups were important for the selective and sensitive determination of Fe^{3+} by forming ground complexes. Further, amine containing groups were the most effective in increasing fluorescence of DSW CDs as well as cellulose CDs indicating that further research should be done to identify the potential of nitrogen doped CDs.

Chapter 4 Nitrogen-doped durian shell derived carbon dots

Herein, a facile one-pot hydrothermal process is used to develop nitrogen-doped carbon dots (NCDs) with durian shell waste as the precursor and Tris base as the nitrogen doping agent. The synthesized NCDs showed a quantum yield of 12.93% with a blue fluorescence under UV-light irradiation and maximum emission at 414 nm at an excitation wavelength of 340nm. XPS and FTIR spectroscopy showed the presence of nitrogen and oxygen functional groups on the NCD surface. The particles were quasi-spherical with an average particle diameter of 5 nm. The synthesized NCDs were resistant to photobleaching and stable under a wide range of pH but was negatively affected by increasing temperature. NCDs showed high selectivity to Tetracycline as the fluorescence of NCDs was quenched significantly by Tetracycline as a result of the inner filter effect. Based on sensitivity experiments, a linear relationship ($R^2=0.989$) was developed over a concentration range of 0-30 μM with a detection limit of 75 nM ($S/N=3$). This study found the resulting NCDs can be used in sensing applications and as a fluorescent ink.

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4.0 Introduction

In the past decade, carbon dots (CDs) have emerged as a novel class of nanomaterials that can be developed through economical and eco-friendly avenues using biomass resources. Conventionally, citric acid, a tricarboxylic acid is often used as the carbon precursor for nitrogen, sulfur, phosphorus dopants including urea [296], tris [153], ethylenediamine [161], phosphoric acid [297], cysteamine [298] and raw sulfur [299] due to the oxygen-rich functional groups like -COOH provided versatile anchoring points for doping agents to improve the performance of carbon dots [268]. Based on the extractive analysis conducted in the previous chapter, it was observed that DSW is rich source of carboxylic acids and phenolic groups albeit the majority is composed of cellulose. In this study, elemental doping with nitrogen is proposed where the nitrogen containing chromophore can act as a surface passivation agent to improve the quantum yield of the synthesized CDs [27]. It is also hypothesized that similar to the effects of citric acid, the presence of carboxylic and phenolic groups in DSW will support successful doping of the CDs. Tris base was used as the doping agent to produce nitrogen doped florescent CDs (NCDs) in a one-pot HTC process. The NCDs are characterised for physical, chemical and optical properties.

CDs provides unique optical and electronic properties including tunable photoluminescence, low photobleaching, aqueous solubility, biocompatibility, and low toxicity [208]. These characteristics have resulted in CDs with diverse applications in the field of novel sensors for the detection of metal ions [25, 121, 208, 300] and organic compounds [301-303]. Apart from these pollutants, CDs can be effectively used as a fluorescent probe for emerging pollutants like antibiotics [304, 305]. With the ever-increasing global antibacterial market, overuse and misuse of antibiotics have led to the dissemination of antibiotic-resistant bacteria which is considered to be a major global

health crisis [306]. Thus, there are increasing demands on developments in analytical techniques for antibiotic screening and detection. The current analytical practices involve high-performance liquid chromatography (HPLC) or mass spectroscopy (MS), capillary electrophoresis and iodometry, albeit these techniques have the downside of using expensive equipments and analytical columns, specialized labour, chemical consumption and high maintenance cost [307]. Thus, developments of novel methods and sensors that are cheaper, faster and greener are important in future efforts of determination of antibiotics.

Thus, in this study, the synthesized NCDs have been tested for selective and sensitive detection of Tetracycline (TC). TC is a broad spectrum antibacterial widely used as a first-line antibiotic in human and veterinary medicine [308]. In recent years, several works have been published in association with tetracycline detection. However, most of these reports include either a complex synthetic process or expensive chemicals. This chapter identifies the potential of using a waste material with naturally existing oxygen functional groups to produce a Tetracycline sensor that shows better or comparable sensing results to these previous reports. The proposed sensing methodology is further validated with two real water systems. This chapter introduces a fast, sensitive and straightforward fluorescent probe to detect TC in an aqueous medium and an efficient fluorescent ink.

4.1 Materials and Methods

4.1.1 Materials and Chemicals

Durian shell was obtained from the local markets in Singapore. Tris base was obtained from Promega Corporation (U.S.). Amoxicillin sodium was purchased from MedChemExpress. (U.S.). Quinine sulfate was purchased from Alfa Aesar. (U.S.).

Dichloromethane, Streptomycin sulfate, Ampicillin sodium, Chloramphenicol, Lincomycin hydrochloride, Tetracycline hydrochloride and sulfanilamide were obtained from Sigma-Aldrich Co. LLC. (U.S.). NaOH was obtained from Merck Pte. Ltd. (U.S.). All chemicals were of analytical grade and used as received.

4.1.2 Synthesis of C-Dots

DSW powder were prepared from ball milling the washed and dried shell waste and then sieving through a 60-80 wire mesh. The NCDs were synthesized by hydrothermal carbonisation of powdered DSW with 0.4 g of Tris base was introduced to 25 ml of DI water. The mixture was transferred to a Teflon-lined autoclave and heated at 210 °C for 12 h. The resulting NCD solution was then allowed to cool naturally to room temperature and then filtered with a 0.45 µm filter followed with 0.22 µm filter membranes to remove the larger particles. The solution was then washed with dichloromethane to remove any unreacted organic moieties and subjected to dialysis against deionized (DI) water through a dialysis membrane (3500 MWCO) for 48 h before use. The produced NCD solution was stored at 4 °C until characterisation.

4.1.3 Characterisation

Fluorescence spectra were acquired with the Agilent Cary Eclipse Fluorescence Spectrophotometer (USA). Ultraviolet-Visible absorption spectra were recorded with a Varian Cary 50 UV/Vis Spectrophotometer (USA). Time resolved fluorescence spectroscopy was done with Horiba fluorolog-3 spectrofluorometer (Japan) equipped with a 360nm nanoLED. Fourier transform infrared spectroscopy (FTIR) was measured with a Bruker Tensor 27 FTIR spectrophotometer (USA). Transmission electron microscopy (TEM) was performed on a JEOL JEM-1400 (Japan). Raman pattern was

obtained with the HORIBA XploRAPLUS Raman Microscope (Japan). X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Kratos Analytical AXIS Supra photoelectron spectrometer (UK). X-ray Powder Diffraction (XRD) was performed on a Bruker D8 Advance (USA). Quantum Yield (QY) measurements were done using quinine sulfate as the reference and the detail procedure is given in section 2.5 of chapter 3.

4.1.4 Fluorescence Measurement

All fluorescence measurements were done at room temperature in DI water. To assess the selectivity, Amoxicillin, Streptomycin, Chloramphenicol, Sulfanilamide, Lincomycin, Tetracycline and Ampicillin were evaluated with the NCDs. In a typical assay, final NCD concentration was maintained at 125 $\mu\text{g/ml}$ while the antibiotic concentration was 100 μM . The PL spectrum was recorded at an excitation wavelength of 340 nm. All measurements were performed in triplicates. Two different water samples (Jurong Lake water and tap water) were used to validate the proposed TC sensor. All water samples were filtered with 0.22 μm syringe filter membranes to remove particles. Subsequently, 2 ml of the real water samples were spiked with known concentrations of TC and exposed to 125 $\mu\text{g/ml}$ NCD. The fluorescence emission spectra were analyzed at an excitation wavelength of 340nm.

4.2 Results and Discussion

4.2.1 Characterisation of NCD

Characterisation tests were conducted to get insights into the PL mechanism of the NCDs. The functional groups of the synthesized NCDs were evaluated by the FTIR spectrum together with the undoped CDs (Figure 4-1). The broad absorption peak at

3413 cm^{-1} and 3243 cm^{-1} corresponds to the N-H and phenolic-OH stretching vibrations [121]. Compared to the FTIR spectrum of undoped CDs, NCDs peaks around 3000-3500 cm^{-1} is broader and shifted towards 3500 cm^{-1} indicating the presence of stronger N-H stretching vibration of amine bonds due to the doping [272]. The absorption peak at 2916 cm^{-1} and 2815 cm^{-1} were assigned to the C-H stretching vibrations [208, 247]. The absorption at 1750 cm^{-1} and 1650 cm^{-1} corresponds with -C=O- (carboxylic acid) and C=N functional groups, respectively [121]. The band at 1200 cm^{-1} represents the C-O-C group [247] while the stretching vibration bands at 1090 cm^{-1} indicates -C-O oxygen containing functional groups including carboxyl groups [208]. The -C=O, -C=C, -C-O-C and -C-O peaks of undoped CDs are more prominent compared to the NCDs. These results are consistent with previous studies and is attributed to the gradual removal of oxygen functional groups by the successful doping of nitrogen [309, 310]. Overall, the presence of these oxygen and nitrogen containing functional groups improved the dispersibility of NCDs in water by enhancing the hydrophilicity [172].

Figure 4-1: FTIR Spectra of the NCDs and CDs

Raman spectroscopy (Figure 4-2a) indicated two vibrational peaks, at 1380 and 1607 cm^{-1} , which corresponded with disordered (D) structures in graphene and graphitic (G) bands respectively [125]. The ratio of D and G peak intensities (I_D/I_G) was around 1.42, which suggested the NCDs produced had high surface defects compared to the sp^2 graphitic structure. Further, the XRD patterns were used to confirm the crystalline phase of the synthesized NCDs as shown in Figure 4-2b. The peak at 16° showed the presence of disordered carbon [246] and the broad diffraction peak around 22° which corresponded with a carbon lattice spacing of 3.99 Å was slightly higher than the (002) lattice spacing of 3.44 Å [247]. This increment was attributed to the increase in the amorphous nature of the NCD surface [311].

Figure 4-2: (a) Raman Spectra and (b) XRD Spectra of the NCDs

TEM imaging was employed to view the particle morphology and size distribution of the NCDs. Results indicated the NCDs were well dispersed (Figure 4-3a), and shape of the NCDs was quasi-spherical. The average diameter of the particles was measured to be 5 nm (Figure 4-3b).

Figure 4-3: (a) TEM images of the NCDs and (b) particle diameter distribution

Figure 4-4: (a) XPS spectrum of the NCDs, (b), (c), and (d) High-resolution C1s, O1s, and N1s XPS spectra of the NCDs

Figure 4-4a represents the XPS survey spectrum conducted for C, O, N elements on the NCDs. The corresponding elemental composition were 75.32%, 22.35% and 2.33%, respectively. The high resolution C1S spectrum shown by Figure 4-4b is deconvoluted into three peaks at 284.8, 286.5 and 288.3 eV, which is attributed to C-C/C=C, C-O and C=O bonds, respectively [20, 275]. The O1s spectrum (Figure 4-4c) was resolved to two peaks at 531.7 and 532.9 eV, which are due to C-O and C-OH/C-O-C groups, respectively [208]. The N1s spectrum (Figure 4-4d) was deconvoluted to three peaks at 397.5 eV for C≡N, 399.7 eV for C-N and 400.9 eV for N-H bonds [208, 312]. Thus, XPS results further confirmed the presence of oxygen and nitrogen functional groups on the synthesized NCDs.

Figure 4-5a illustrates the UV/vis absorption spectrum of NCDs with the maximum excitation and emission spectra. Three peaks in the absorption spectra can be observed at 254 nm, 280 nm and 320 nm. The former two peaks correspond with the aromatic π system or the $n-\pi^*$ transition of the carbonyl group while the peak at 320 nm is due to the trapping of excited state energy by the surface states [126]. The maximum photoluminescence was observed at 414 nm upon excitation at 340 nm.

Inset of Figure 4-5a shows the synthesized NCD solution exhibited a bright blue colour under a UV light of 365 nm which was transparent yellow under daylight. QY of the NCDs was calculated to be 12.93% which was two times compared to the undoped CDs. The synthesized NCDs exhibited excitation dependent emission between 320-440 nm which is shown in Figure 4-5b, and this was attributed to the presence of trap states arising from the surface defects [43, 277]. The NCD solution was used as a fluorescent ink directly without any pretreatment as shown in Figure 4-5c. The

photographs show the text was distinct from the background under UV light and so suggested the NCDs can be material for fluorescent ink.

Figure 4-5: The optical properties of the NCDs. (a) UV/Vis absorption spectrum with maximum emission and excitation spectra, (b) PL emission spectra of NCDs at different excitation wavelengths and Photographic image of a text written fluorescent ink under (c1) normal indoor light and (c2) UV-light

To investigate the applicability of the synthesized NCDs as a fluorescent probe, the stability of the NCDs dispersed in water was evaluated by measuring the PL intensity variation with pH, temperature, and time. Under varying pH values from 3 to 11 (Figure 4-6a), the maximum PL intensity was recorded at a pH = 5. However, the overall intensity variation was within a relative standard deviation (RSD) of 2.1%. Thus, it can be considered the NCDs were resistant to pH variation.

Figure 4-6: The PL variation of NCDs with (a) solution pH, (b) Ionic content, (c) Temperature and (d) photostability under continuous UV irradiation

Similar to pH, the fluorescent intensity was very stable with ionic strength (Figure 4-6b). At a salt concentration of 500 mM, the PL intensity dropped only by 3% indicating

the resistance the fluorescent intensity to the ionic concentrations in the environment. In contrast, the intensity variation with temperature was significant where lower temperatures had higher fluorescent intensity (Figure 4-6c). The temperature dependent fluorescence was attributed to thermal activation of non-radiative trappings in surface and defective sites [282]. The photostability of NCDs was also quantified by continuous exposure to UV irradiation (Figure 4-6d) and the intensity was preserved at 97% of its initial value after continuous exposure to UV irradiation by Hg lamp for 120 mins, suggesting the high photostability of the synthesized NCDs.

4.2.2 Mechanism and detection of antibiotics

To investigate the influence of antibiotics to the photoluminescence property of NCDs, First, the selectivity towards different antibiotics including Lincomycin (Lin), Tetracycline, Amoxicillin (Amox), Ampicillin (Amp), Streptomycin (Str), Sulfanilamide (Sulf) and Chloramphenicol (Chlo) was investigated (Figure 4-7) and the results indicated that NCDs had strong sensitivity towards TC with a fluorescent quenching around 80% and moderately sensitive towards Amoxicillin with fluorescent enhancement around 16% at an antibiotic concentration of 100 μ M.

Figure 4-7: Selectivity of NCDs towards different antibiotics

The sensitivity of NCDs fluorescence quenching to TC was further evaluated with various concentrations of TC. The fluorescence intensity declined gradually with the increase of TC concentrations ranging from 0 to 100 μM (Figure 4-8 a and b). A good linear regression correlation was found as below:

$$Y = 0.0241 X - 0.419$$

with a correlation coefficient R^2 of 0.989 over the concentration range 0-30 μM .

Figure 4-8: (a) Fluorescent intensity with TC concentration and (b) PL emission spectra with increasing TC

The lowest detection limit (LOD) was calculated to be 75 nM based on a signal to noise ratio of 3 and as seen on table 4-1, the performance of TC sensing was better or comparable with previously reported fluorescent probes.

Table 4-1: Comparison of TC detection with other reported probes in recent years

Fluorescent Probe	Linear Range (μM)	LOD (nM)	Ref.
Europium-doped CDs	0.5-200	300	[313]
Citric acid and glutathione CDs	2-150	520	[314]
Polymer imprinted CDs	0.02-40	5.48	[164]
Silica imprinted CDs	0.1-50	9.0	[315]
Cadmium telluride quantum dots	13.4-134	308	[316]
Molecularly imprinted polymer ZnO nanorods	2-120	127	[317]
Nitrogen doped Durian shell waste CDs	0–30	75	This work

To explore the sensing mechanism of TC, a series of studies were carried out. According to Figure 4-9a, there is a good spectral overlap of the absorption spectrum of TC with the excitation spectra of the NCDs compared to other antibiotics. This indicated the quenching could happen by inner filter effect (IFE) or/and Förster resonance energy transfer (FRET) process. However, the lifetime of the NCDs in the presence and absence of TC remained unchanged (Figure 4-9b) and was measured to at 5.8 ns. Thus, it was reasonable to exclude FRET as a possible mechanism in TC quenching.

Further, the absorption spectra of the NCDs, NCDs with TC and TC were examined (Figure 4-9c) and there was no difference in the NCD absorption spectra when TC was added. This confirmed the absence of ground state complex formation. Thus, the IFE served as the primary quenching mechanism for NCDs in the presence of TC. In recent years, IFE based sensors have gained more attention due to their simplicity and flexibility as these have no requirement for electron or energy transfer processes or any

covalent linking between the fluorophore and quencher [314]. Thus, the synthesized NCDs provided a highly selective, sensitive and simpler sensing platform to detect TC.

Figure 4-9: (a) Normalised UV-Vis adsorption of antibiotics with excitation and emission spectra of NCDs, (b) Time-correlated single-photon counting (TCSPC) of NCDs in the presence and absence of TC and (c) UV-Vis adsorption for TC, NCDs and NCDs with TC

To validate the sensing parameters of TC with NCDs, experiments were conducted on actual water samples. The water samples were spiked with known concentrations of TC

and the recovery percentages and relative standard deviations (RSD) are as shown in Table 4-2.

Table 4-2: Detection of TC in actual water samples (n=3)

Sample	Spiked Concentration (μM)	Measured Concentration (μM)	Recovery %	RSD %
Lake Water	5.00	5.04	100.86	3.42
	10.00	10.85	108.46	2.52
	20.00	20.91	104.54	0.69
Tap Water	5.00	5.31	106.28	0.92
	10.00	10.51	105.11	0.79
	20.00	19.72	98.62	1.56

As expected, the fluorescence decreased with increasing TC concentration and the recoveries were between 98.6 -108.5% while the RSD was below 3.5%. This reinforced the argument NCDs is a promising sensor to detect TC in environmental water samples.

4.3 Conclusion

Blue-emitting nitrogen doped NCDs could be successfully synthesized using a one-pot hydrothermal method using durian shell waste with tris base as the doping agent. The presence of natural existing oxygen groups in the durian shell provided versatile anchoring points for the nitrogen dopant which resulted in carbon dots with good fluorescent properties and stability. Thus, durian shells can possibly be an effective and cheap carbon precursor material for future CD development. The synthesized NCDs exhibited high selectivity towards TC based on the IFE process. The IFE based sensing strategy would provide an efficient, convenient and sensitive technique to detect TC while avoiding any complex covalent bonding. Thus, the synthesized NCDs holds broader applicability in TC detection in biological and environmental systems.

Chapter 5 Metal co-doped carbon dots from cellulose biomass

Development of metallic and nonmetallic heteroatom doped carbon dots have gained attention due to their enhanced physicochemical and photoluminescence properties. In this study, a facile one pot hydrothermal carbonisation approach was taken to synthesise nitrogen, aluminum co-doped carbon dots (N/Al-CDs) with a photoluminescence quantum yield of 28.7%. Durian shell, a cellulose biomass waste, was used as the primary carbon source and compared to previously reported cellulose based carbon dots, this study presents one of the highest quantum yields. The structural and fluorescent properties of the synthesised N/Al-CDs were characterized through XPS and FTIR. The maximum emission was at 415 nm upon excitation at 345 nm. The synthesised N/Al-CDs were resistant to photobleaching and highly photostable within the pH, ionic strength and temperature variations investigated. TEM images showed particles were quasi-spherical and well dispersed with an average diameter of 10.0 nm. Further, the N/Al-CDs was developed as a fluorescence sensor for highly selective and sensitive detection of Mn^{7+} ions. A linear relationship was developed over a concentration range of 0-100 μM while the limit of detection was 46.8 nM. Application of the sensor for detection of Manganese (VII) to two real water samples showed RSDs were less than 3.9% and 1.3%, respectively.

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5.0 Introduction

Zero-dimensional carbon nanodots is a recent addition to the functional nanomaterial family and currently, it is establishing as an advance nanomaterial in many applications including environmental monitoring, photocatalysis, bioimaging, and energy storage [118, 318, 319]. Photoluminescence (PL) is a key characteristic of CDs and developments have been made to increase PL by size control, surface functionalization/passivation, and heteroatoms doping [320, 321]. Due to the facile synthesis process and the high tunability of the CDs, heteroatoms doping with one or a combination of nitrogen, sulfur, boron and phosphorous doping agents is a common synthesis method in CD production [322-324]. Introduction of atomic dopants generated n-type or p-type carriers which changed the electronic and optical properties associated with the HOMO-LUMO energy gap [68]. Thus, controlled doping can greatly enhance the quantum yield. Recently metal dopants have been used for CD production with Cu-CDs produced with sodium citrate and cuprous chloride for Fe^{3+} sensing [325], Zn-CDs produced with sodium citrate and zinc chloride for glucose [326], and cholesterol and xanthine sensing using N-Cu CDs produced by hydrothermal reaction between citric acid and copper acetate [327], and Mn coordinated CDs for cell imaging [328]. Compared to the non-metals, the use of metals increased the electron density in CDs which then increased the electronic transitions for improved optical properties [329]. Further, introducing metals to the carbon matrix elevated electronic mobility to improve the physiochemical properties of CDs [326, 329].

In this study, durian shell waste (DSW) together with urea and aluminum nitrate were used for the first time in a facile hydrothermal reaction to produce N/Al-CDs. In the previous chapter DSW was successfully doped from nitrogen due to the presence of many anchoring points provided by the oxygenated functional groups. In this study it

is hypothesized, these groups will still be effective in doping metals and thereby increase the doping efficiency leading to a higher photoluminescence [147, 330]. According to the results, the synthesised N/Al-CDs were highly fluorescent with a quantum yield (QY) of 28.7% whilst the metal free N-CDs QY was only 10.4%. PL of the N-Al co-doped DSW based CDs was much higher than values previously reported for cellulose based CDs where the QYs were 7.6% for corn stalks [208], 6.9% for pomelo peels [5] and 9.2% for wheat straw [244]. Moreover, The values in this study are comparable with Zn doped sodium citrate CDs and Gd-ethanediamine doped citrate acid which had QYs of 32.3% and 21%, respectively [326, 331]. Considering the low PL typically shown by cellulose based CDs, the proposed method suggested a potentially viable avenue to develop future cellulose CDs. The synthesized CDs were used as a ratiometric sensor to detect Mn^{7+} in water.

More than 80% of the Mn^{7+} ion (in the form of permanganate (MnO_4^-)) used in the drinking water treatment industry is to remove dissolved iron and manganese, hydrogen sulfide and control taste and odour [332]. It is also used as a bleaching agent, treatment of sewage sludge, and as a biocide to control fungi and algae [332, 333]. However, such usage can lead to Mn^{7+} residuals – e.g. in the drinking water after filtration which can lead to discoloration and metallic taste, skin irritation and gastrointestinal distress [332]. Given the recurrent usage, various techniques have been developed to detect Mn^{7+} over the years. These methods are primarily based on titration with high purity chemicals like sodium thiosulfate/iodide and sodium oxalates in the presence of strong acids [334, 335]. Apart from harmful chemicals, these methods are time consuming and the accuracy of the results are highly sensitive to the environmental conditions (e.g. pH, temperature) [336]. Thus, efficient identification of the presence of Mn^{7+} is important in regulating water quality.

This chapter reports a facile one-step hydrothermal carbonisation method to synthesize highly fluorescent carbon dots from DSW by co-doping with an aluminum-nitrogen mix. The N/Al-CDs were characterised structurally and optically to assess the presence of dopants and their impact on the quality of carbon dots. Finally, the N/Al-CDs were used to develop a ratiometric sensor with MnO_4^- (denoted by Mn^{7+}) concentration. This relationship was verified using real water systems.

5.1 Materials and Methods

5.1.1 Materials

DSW was obtained and powdered according to [38]. Urea, $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, NaOH and NaCl were obtained from Merck Pte. Ltd, US. KMnO_4 , $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, ZnCl_2 , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were obtained from Sigma-Aldrich Co. LLC, US. Quinine sulfate and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were purchased from Alfa Aesar, US. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ were purchased from Sinopharm Chemical Reagent Co. Ltd, China. All the chemicals were of analytical grade and used as received without further purification.

5.1.2 Synthesis of N/Al-CDs

Hydrothermal carbonisation was used to synthesise N/Cu-CDs. Finely ground DSW (1g) powder (0.22 mm mesh), 0.1g Urea and 0.1g of Aluminum nitrate was mixed with 25ml of deionized (DI) water and sealed into a 45ml Teflon-lined stainless steel autoclave and heated at 210°C for 12h. The heating rate was maintained at $5^\circ\text{C}/\text{min}$.

After the mixture was cooled to room temperature, the CD particles were separated and purified according to method described in Jayaweera et al [319]. For comparison, N-CDs were prepared via the same method except for the addition of Aluminum nitrate.

5.1.3 Characterisation

Fourier transform infrared spectroscopy (FTIR) was performed with a Bruker Tensor 27 FTIR spectrophotometer. Elemental mappings of CDs were done with a JEOL JSM 7200F field emission scanning electron microscope (FE-SEM). Morphology and the crystallin structures of CDs were viewed on a JEOL 2010 transmission electron microscope (TEM) under 200kV. Kratos Analytical AXIS Supra photoelectron spectrometer was used for X-ray photoelectron spectroscopy (XPS) measurements. Fluorescence spectral measurements were performed on an Agilent Cary Eclipse Fluorescence Spectrophotometer. Fluorescent decay curves were obtained from a Horiba fluorolog3 spectrofluorometer equipped with a 360nm nanoLED. Ultraviolet-Visible (UV-Vis) absorption spectra were determined with an Agilent Varian Cary 50 UV/Vis Spectrophotometer. Quantum Yield (QY) measurements were done at 345 nm using quine sulfate reference solution as explained in [319]. The absorbance was kept less than 0.05 to minimize reabsorption.

5.1.4 Detection of Mn^{7+}

The sensitivity of Mn^{7+} ions was determined by mixing 60 μL of CD solution (125 $\mu\text{g}/\text{ml}$) with the various Mn^{7+} ion solutions with concentrations from 0 to 180 μM to reach a total volume of 2 ml. Each assay was mixed thoroughly and kept for 15mins at room temperature before recording the PL intensity at an excitation wavelength of 345 nm. Ca^{2+} , Cr^{3+} , Ni^{2+} , La^{3+} , Fe^{2+} , Fe^{3+} , Ce^{3+} , Cr^{6+} , Pb^{2+} , Na^{+} , Mg^{2+} , Zn^{2+} , Cu^{2+} and Co^{2+} ions with a metal ion concentration of 100 μM . All measurements were performed in triplicates.

5.2 Results and Discussion

5.2.1 Characterisation of N-Al CDs

Functional groups on the surface of N/Al-CDs and N-CDs were characterised with ATR-FTIR and shown in Figure 5-1. The broad absorption peak at 3310 cm^{-1} corresponded to the phenolic-OH and N-H stretching vibrations [319]. The absorption peak at 2960 cm^{-1} and 1380 cm^{-1} were ascribed to the C-H stretching and bending vibrations, respectively [133]. Peaks at 1600 cm^{-1} and 1450 cm^{-1} corresponded to the $\text{sp}^2\text{ C}=\text{C}$ bending and $\text{sp}^3\text{ CH}_2$ bands, respectively [208]. The vibration bands at 1275 cm^{-1} and 1050 cm^{-1} in the N-CDs corresponded with the C-O cm^{-1} stretching bond [127] while the peak at 1150 cm^{-1} corresponded with -C-N stretching vibration [272].

Figure 5-1: FTIR Spectra of N-CD and N/Al-CDs

The affinity of Al to bond with oxygen functional groups was further corroborated when the presence of aluminium on the N/Al-CDs was confirmed by the bands at 1070 cm^{-1} and 740 cm^{-1} which were ascribed to the Al-O-H and Al-O bonds, respectively [337]. These hydroxyl and nitrogen functional groups increased hydrophilicity and thus improved the solubility of N/Al-CDs in water [172]. Raman spectroscopy (Figure 5-2a) indicated two vibrational peaks, at 1360 cm^{-1} and 1580 cm^{-1} , and these were attributed to the disorderly network of sp^2 carbon clusters (D) and graphitic (G) bands,

respectively [338, 339]. The spectrum was fitted with a double Gaussian function and the integrated areas of the respective curves were used to calculate an I_D/I_G ratio of 1.22. This suggested the synthesised N/Al-CDs had high surface defects compared to the sp^2 hybridized graphene structure.

Figure 5-2: (a) Raman Spectra N/Al-CDs, (b) TEM and the HRTEM (inset) images and (c) Particle diameter distribution histogram of N/Al-CDs

Morphology and structure analysis of the CDs was performed with TEM imaging as shown in Figure 5-2b. The N/Al-CDs were quasi-spherical and well separated indicating an even aqueous distribution of CD particles in the solution. The inset on Figure 5-2b shows a structured crystallinity with a lattice spacing of 0.24nm correlated to (100) the in-plane graphene structure [340]. The diameters of CDs ranged from 6-14nm with an average particle size of 10nm (Figure 5-2c). EDS elemental mapping distribution of carbon, oxygen, nitrogen and aluminum (Figure 5-3) further indicated the elements were evenly distributed on the CD surface.

Figure 5-3: Elemental mapping of CDs showing carbon (purple), oxygen (green) nitrogen (blue) and aluminum (yellow)

Elemental composition of the CDs was analysed by XPS and full scan spectrum (Figure 5-4a) showed four dominant peaks attributed to C1s (79.05%), O1s (16.58%), N1s (2.71%) and Al 2p (1.66%) indicating successful integration of aluminum and nitrogen to the CDs. The high resolution C1S spectrum (Figure 5-4b) indicated three binding energies at 284.8, 285.78 and 288.3 eV. This corresponded to the C-C/C-H, C-O/C-N, and C=ONH/C=OO- bonds, respectively [20, 341]. The N1s spectrum (Figure 5-4c) showed three peaks at 395.9, 397.5 and 399.1 eV which were attributed to the N-O, Al-N and Pyridine N bonds, respectively [342, 343]. The binding energy spectrum of Al 2p showed (Figure 5-4d) three peaks at 73.2, 73.8 and 74.4 eV which corresponded to Al-N, Al-O and Al-OH, respectively [344, 345]. These results are further

corroborating the FTIR results and indicate that the Al^{3+} had coordinated with oxygen and nitrogen groups.

Figure 5-4: (a) XPS spectrum of the N/Al-CDs with High-resolution (b) C1s, (c) N1s and (d) Al 2p (f) spectra

5.2.2 Optical Properties of N-Al CDs

The optical properties of the N/Al-CDs were investigated with UV-vis absorption and fluorescence analysis. The UV absorption spectra (Figure 5-5a) showed a strong peak at 264 nm and a weak peak at 305 nm. The former peak corresponded with the π - π^* transitions of aromatic sp^2 domains [346] while the weak peak at 314 nm corresponded with the $\text{n}-\pi^*$ transition of the $\text{C}=\text{O}/\text{C}=\text{N}$ groups [347]. As shown in Figure 5-5a inset, the N/Al-CDs emitted a bright blue fluorescence under a 365 nm UV light which is attributed to the intrinsic near band edge electron hole recombination in the sp^2 cluster

[327]. Further, the maximum photoluminescence was observed at 415 nm upon excitation at 345 nm.

Figure 5-5: (a) UV/Vis absorption spectrum with maximum emission and excitation spectra and a photograph of N/Al-CDs under 365 nm UV light (inset) and (b) PL emission spectra of N/Al-CDs at different excitation wavelengths

Figure 5-5b presents the fluorescence emission spectra of N/Al-CDs at different excitation wavelengths. Two distinctive regions could be observed where excitation independent emission was observed from the 300-345 nm excitation and an excitation dependent emission from 350-420 nm excitation. Several mechanisms have been reported to explain CDs emission but the exact mechanism is yet to be decided [66]. Based on the literature, the emission of N/Al-CDs could be due to the combined effects of emissions resulting from the π - π^* transitions of the sp^2 clusters and the surface functional groups [66, 327]. The initial excitation independent emission was primarily governed by the single recombination of electron-hole pairs in the sp^2 cluster. However,

at higher wavelengths, the energy would be insufficient to excite these sp^2 clusters and the emission of N/Al-CDs would then have been dominated by the surface trapping states which introduced new energy band gaps on the N/Al-CDs resulting in excitation dependent emission after 350nm [180, 327].

In addition to the fluorescence spectrum, the stability of the N/Al-CDs was investigated by measuring the variation of PL intensity against pH, temperature, ionic strength and photobleaching. The variation is interpreted by the mean normalized intensity (MNI) and the relative standard deviation (RSD). N/Al-CDs showed high stability under varying pH level from 3-11 (Figure 5-6a) with an MNI of 0.989 and an RSD of 2.17%. The PL change with ionic strength was measured by exposing the synthesised CDs to increasing concentrations of NaCl solutions up to 500mM (Figure 5-6b). N/Al-CDs exhibited high resistance to the ionic strength with an MNI of 0.96 and an RSD of 3.02%. Similarly, the resilience of CDs to temperature variation was also high (Figure 5-6c) with an MNI of 0.97 and an RSD of 3.54%. Despite the stability, it could still be observed that PL intensity decreased slightly with increasing temperature. This could be attributed to thermal activation of non-radiative trappings in surface and defective sites [282, 319]. Finally, the photostability was measured by continuous exposure to UV irradiation by a Hg lamp (Figure 5-6d). PL intensity of N/Al-CDs only reduced by 8% and 14% after continuous exposure of up to 60 mins and 120 mins, respectively indicating high resistance to photobleaching [130]. Thus, it can be concluded that the synthesised N/Al-CDs had positive fluorescent properties with good optical stability.

Figure 5-6: (a) Effect of pH, (b) Effect of chloride concentration, (c) effect of temperature and (d) photostability under continuous UV irradiation on the PL intensity of N/Al-CDs measured at 345 nm excitation

5.2.3 Detection of Mn (VII)

In this study, the excellent water solubility and the optical stable characteristics of N/Al-CDs were used to detect dissolved Mn^{7+} concentrations in water to develop a sensitive and selective fluorescent nano-probe. The selectivity of N/Al-CDs towards sensing Mn^{7+} was investigated by comparing the effects on fluorescence in the presence of different metal ions (Figure 5-7a). N/Al-CDs fluorescence was quenched nearly 85%

with the introduction of Mn^{7+} whereas the intensity of other metals except Fe^{3+} and Cr^{6+} was only affected by $\pm 5\%$. From chapter 3, undoped DSW based CDs showed high selectivity towards Fe^{3+} . This was ascribed to Fe^{3+} complex formation with oxygen groups [38]. However, the introduction of N-Al doping mix has reduced the quenching effect to only 20% which was attributed to the formation of Al-O bonds that subsequently reduced the Fe^{3+} ground state complex formation with oxygen groups. The Cr^{6+} ion quenched 40% of the fluorescence due to inner filter effects which will be discussed later in this section. Nevertheless, quenching effects with Mn^{7+} is highly significant and thus, the N/Al-CDs has improved selectivity towards Mn^{7+} . To further quantify the fluorescence quenching, measurements were taken for a series of Mn^{7+} concentration from 0 to 180 μM (Figure 5-7b). Quenching efficiency was calculated by $[(I_0/I)-1]$ where the I_0 and I are fluorescence intensities in the absence of presence of quencher, respectively. A linear relationship of $[(I_0/I)-1] = 0.0635 [\text{Mn}^{7+}] - 0.2601$ was observed (inset of Figure 5-7b) in a range of 0-100 μM with a good correlation coefficient ($R^2=0.9943$, $n=3$).

Figure 5-7: (a) Selectivity of N/Al-CDs towards different metal ions and (b) Relationship between quenching efficiency against Mn^{7+} concentration

The calculated limit of detection (LOD) was 46.8 nM in which $LOD = 3\delta/s$, where δ is the standard deviation of ten blank samples and s is the slope of the linear relationship. According to the US EPA guidelines, the recommended short term exposure level of Mn^{7+} is 22.1 μM while the drinking water quality intended to control discolouration, staining and bitter metallic taste is maintained at 1.1 μM [332]. Since the LOD of the nanoprobe is significantly below these targeted levels, it was a promising candidate for the detection of Mn^{7+} in water samples.

To identify the sensing mechanism, further experiments were conducted. Generally, quenching of fluorescence in the presence of a quencher would occur due to either formation of non-radiative ground state complexation or by Förster resonance energy transfer (FRET) or the inner filter effect (IFE) or photoinduced electron transfer from (PET) from N/Al-CD to Mn^{7+} [348]. There is a considerable spectral overlay between the absorption spectra of Mn^{7+} and excitation spectra of N/Al-CDs (Figure 5-8a) which indicated the possible involvement of the FRET or IFE mechanism. However, absorption spectrums of other metals with the excitation/emission spectrum shows the direct overlap of Cr^{6+} ion. It is concluded that this overlap by Cr^{6+} was responsible for the quenching of ~40% of CD fluorescence through IFE as reported by Tan et al [349]. However, the overall quenching efficiency for Mn^{7+} was significantly higher compared to Cr^{6+} . This indicates the presence of another dominant mechanism. To ascertain if the quenching was induced by FRET, time-resolved fluorescence lifetime spectra (Figure 5-8b) were studied. After fitting the spectra with a double-exponential function, the average decay time was measured to be 1.60 ns ($\chi^2 = 0.85$) and 1.68 ns ($\chi^2 = 0.87$) in the absence and the presence of the quencher Mn^{7+} , respectively. The almost identical decay times could reasonably eliminate the FRET mechanism.

Figure 5-8: (a) Normalised UV-Vis adsorption spectra with metals and maximum excitation and emission spectra of N/Al-CDs and (b) Time-correlated single-photon counting of N/Al-CDs in the presence and absence of Mn⁷⁺

Figure 5-9a shows the UV-Vis spectra of N/Al-CDs, Metal, N/Al-CDs -Metal system and the sum absorption spectrum between N/Al-CDs and Metal for Mn⁷⁺. It could be observed the CD-Mn⁷⁺ complex absorption spectrum did not superimpose with the sum of CD and Mn absorption spectra. CDs are a rich source of pi bonds and this is further confirmed by the strong peak corresponding to C=C bond in the FTIR spectra. It is expected that Mn⁷⁺ coordinates with the alkenes and upon photoexcitation the excited state electrons undergo redox reaction by reducing Mn⁷⁺ to Mn⁴⁺ [350]. This was further confirmed by the visible colour change of the purple Mn⁷⁺ to brown Mn⁴⁺ upon the addition of CDs (Figure 5-9a inset). However, CD- Cr⁶⁺ complex did not deviate from the sum of CD and Cr⁶⁺ absorption spectrum indicating the absence of electron transfer complex formation (Figure 5-9b). Thus, the non-radiative PET oxidative transfer process has dominated the fluorescence quenching process.

Figure 5-9: (a) and (b) UV–visible spectra of N/Al-CDs, Metal, N/Al-CDs -Metal complex and sum of N/Al-CDs and metal absorption spectrums for Mn^{7+} and Cr^{6+} respectively. images of N/Al-CDs with quencher under white and UV ($\lambda_{\text{ex}}=365$ nm) lights (inset 5-9a)

To verify its sensitivity in practical applications, tap water from the Residuals and Resource Reclamation Centre (R3C) Laboratory and lake water from Jurong Lake were used. Lake water was filtered with a $0.45 \mu\text{m}$ filter followed with a $0.22 \mu\text{m}$ filter prior to testing. No Mn^{7+} in the original water samples was detected and the pH was 7.6 and 7.0 for lake water and tap water, respectively. All samples were spiked with a known amount of Mn^{7+} and the recovery percentage and relative standard deviation (RSD) were calculated as shown in Table 5-1.

In both water samples, good recovery percentages were shown with a range from 92.58%-106.16% with an RSD $<3.9\%$ for lake water and $<1.3\%$ for tap water. These results further indicated the reliability and sensitivity of the synthesised N/Al-CDs sensor to detect Mn^{7+} in water samples.

Table 5-1: Detection of Mn^{7+} in tap water and Jurong lake water samples (n=3)

Sample	Spiked Concentration (μM)	Measured Concentration (μM)	Recovery %	RSD %
Lake Water	8.00	7.69	96.25	3.77
	15.00	14.14	94.26	3.86
	20.00	21.23	106.16	3.59
Tap Water	8.00	7.41	92.58	1.19
	15.00	15.88	105.84	0.98
	20.00	20.89	104.45	1.25

5.3 Conclusion

Novel, highly fluorescent carbon dots with a quantum yield of 28.7% were successfully produced by co-doping a durian shell waste with nitrogen and aluminum in a facile one pot hydrothermal carbonisation process. Durian shell waste is primarily cellulose and developing CDs with high quantum yield and excellent photostability provides new opportunities in the future developments of carbon quantum dots and resource recovery from waste. The resulting N/Al-CDs could be used as an efficient fluorescent sensor to detect Mn^{7+} . With high selectivity and a limit of detection at 46.8 nM, the synthesised N/Al-CDs were used in actual water systems to wherein the CDs successfully determined the Mn^{7+} levels. This study presented an efficient and simple method for production of a cellulose based fluorescent nanoprobe Mn^{7+} detection in environmental water systems.

Chapter 6 Conclusion and Future Works

6.1 Conclusion

Use of cellulosic biomass sources as CD precursor materials is gaining attention due to the low cost, ready availability and environment friendly nature. Pure cellulose derived CDs do exhibit low photoluminescence. However, using cellulosic biomass has the advantage of incorporating naturally present heteroatoms (e.g. N, S) and other oxygen groups into the CD structure that can significantly improve the CDs' optical and chemical characteristics. Durian (*Durio zibethinus*), a popular seasonal fruit in Southeast Asia, has a major concern associated with the large quantity of waste in the form of its seeds and shell. The latter accounts for more than 50% of the total fruit. Although there have been studies which investigated the use of DSW as a resource for value added products, the production of such materials involved complex processing and expensive chemicals which hindered sustainable and commercial applications. Thus, this study had aimed to use DSW as a carbon precursor for relatively simple CD production and to apply the synthesized CDs for detecting pollutants in water.

6.1.1 Summary of the Current Work

Initially, a facile one-pot hydrothermal carbonisation process was optimized to synthesize fluorescent CDs from DSW. The analysis of the DSW extractives identified the presence of carboxylic acids, amino acids, amines, alcohols and esters. Among these, the nitrogen containing groups were the most effective in yielding higher fluorescence from CDs. This effect was resonated in pure cellulose based CDs establishing the affinity of cellulose CDs towards nitrogen doping for higher fluorescence. Nevertheless, the oxygen rich surface was instrumental for the selective and sensitive determination of Fe^{3+} by forming ground state complexation with the

analyte. Thus, it can be concluded that DSW is an effective and cheap carbon precursor for CD development and as an efficient fluorescent probe due to the inherent nitrogen and oxygen groups. The former improved the CD quality and the latter enhanced the effectiveness of the application.

Secondly, amine rich tris base dopant produced nitrogen doped CDs from DSW (NCD). The presence of naturally occurring oxygen groups in durian shells provided versatile anchoring points for the nitrogen dopant. Moreover, the incorporation of nitrogen shifted fluorescence to the blue region, doubled the quantum yield and provided higher resistance to photo-bleaching. Thus, it can be concluded that DSW is susceptible to external doping and the physical, chemical, optical characteristics can be tuned and functionalized for a specific type of CDs. In this study, the blue shifted NCDs was used as a highly selective sensor towards an emerging pollutant – Tetracycline based on the inner filter effect (IFE). The IFE based sensing could provide an efficient, convenient and sensitive technique for detection of pollutants since it avoided complex covalent bonds and involved a simple detection method. Nevertheless, easy functionalization enables DSW to be an effectual precursor to produce target specific CDs with tunable photoluminescence.

Finally, highly fluorescent carbon dots with a quantum yield of 28.7% were successfully produced by co-doping durian shell waste with nitrogen and aluminum in a facile one pot hydrothermal carbonisation process. The use of Al increased electron density in CDs and led to higher electronic transitions and mobility. This resulted in one of the highest recorded quantum yields achieved through facile treatment of cellulosic biomass. This further cemented the above conclusion of the efficacy of DSW in producing functionalized CDs through extending the doping agent beyond conventional dopants and successfully including metals. The introduction of N-Al

doping mix reduced sensitivity towards Fe^{3+} and this was attributed to the formation of Al-O bonds that subsequently reduced the Fe^{3+} ground state complex formation with oxygen groups. This concludes that in addition to the optical characteristics and high fluorescence, the Al doping was instrumental in high selectivity towards the targeted analyte and that DSW is highly effective carbon source precursor for CD production for sensing applications.

Other than the increased QY, it should also be noted doping of the raw materials led to the development of CDs with different fluorescence stability. For example, all three products were highly stable under different ionic concentrations and pH levels. However, the fluorescence of NCD was more susceptible to the variation of temperature compared to undoped CDs and metal doped CDs. In addition, the average particle diameter increased with doping which may be due to particle agglomerations caused by differently charged functional groups on the CD surfaces.

Compared to semiconductor quantum dots, which were initially created in the early 1980s, CDs are a recent discovery. Therefore, the availability of CDs in commercial applications is still limited despite the growing research in the area. However, Sigma Aldrich does currently offer CDs that have an emission wavelength of 450-500 nm and a QY of >5% [351]. Further, Nanoshel LLC, a company specializing in commercializing a wide range of nanoparticles, is currently selling surface modified carboxyl CDs with an emission of 460-480 nm and a QY of 36% [352]. Recently, Fuji Pigment Co. Ltd. in Japan has established a large-scale manufacturing plant for carbon quantum dots [353]. These patented CDs have an emission wavelength of 450-500 nm and a QY of 45%. Further, the CDs were targeted towards bio-imaging, protein analysis, cell tracking, and many other biomedical applications given the biocompatible precursors like glucose and amino acids used in the process [353]. This study has

contributed to develop DSW based CDs that has a QY of 29% that is highly stable under various environmental conditions. Given the availability and abundance of many cellulose based biomass sources (unlike the more valuable glucose and amino acids), this study has set the foundation for further developments in cellulose CDs that has the potential to develop low cost, environmentally friendly nanostructure manufacturing process.

6.1.2 Challenges and Future Work

Although this study has proven DSW to be a highly effective precursor to produced tunable CDs, proposals described in the following section can improve the quality of CDs further and increase the feasibility of using DSW as a precursor material for CD production.

- Scaleup and Commercialization

Despite the potential in delivering high quality CDs, durian shells are indeed generated seasonally. In Singapore, the peak season occurs between from June to September while there is a minor season from December to February. For this study, Durian shells were oven dried and stored in sealed containers until used and such storage may be an approach to bridge the low season of five months. However, if the cost of such storage is prohibitive (possibly not if dried durian shells are bunkered), it is suggested to evaluate the dopants developed in this study acting on other cellulosic biomass materials and subsequently introduce a portfolio of cellulosic biomass that can be used to synthesize quality CDs.

To further strengthen the commercialization of biomass CDs, it is important to develop CDs with a diverse range of emission spectrums. This study has proven that surface

modification and heteroatoms doping have a direct impact on the fluorescent enhancement and produce CDs that have approximately similar QY of commercialized CDs. Although this has provided a strong foundation for the use of cellulose biomass as a precursor material, future studies can be conducted to include advanced dopants like polymer materials and organic fluorophores. Furthermore, these studies should also determine the effects of such doping to the carbon core and surface structure as well as to the optical, physical and chemical characteristics of CDs.

- Diversified Applications

This study identified the CDs produced from DSW are of high quality, resistant to external environmental conditions and can be easily functionalized for desired characteristics. Moreover, the synthesised CDs were efficiently applied as a fluorescent sensor for Fe^{3+} , Mn^{7+} and Tetracycline. However, broadening the possible applications of CDs has an inherent advantage on the market value of the CDs. Thus, further developments can be studied both in the sensing field as well as others. As explained previously, CDs can be modified with advanced doping agents to produce nanostructures with varying emission centers. These different CDs can be applied as sensors for a broader range of pollutants and other biological substances. Further, CDs in the NIR emission are favored in the bioimaging fields due to the deep tissue penetration, low light damage to bio tissues and minimal autofluorescence.

Moving beyond the sensor applications, this study has shown that the CDs can be used as a fluorescent ink. Considering the high QY and photostability, the synthesised CDs can be developed as counterfeit detection markers or even food grade fluorescent markers. Finally, the successful doping of aluminium into the CD matrix indicate the

potential of future CD developments with various metal complexes. This phenomenon can be used to develop CDs with embedded metal catalysts that can be used in photocatalytic applications including pollutant degradation reactions and photocatalytic chemical reactions. Thus, if studied successfully, such developments would make this cellulose biomass a potentially important precursor in commercial productions.

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Appendix

List of Publications

Journal Articles

- 1) Jayaweera, S., Ke, Y., Hu, X. and Ng, W. J. Facile preparation of fluorescent carbon dots for label-free detection of Fe^{3+} , Journal of Photochemistry and Photobiology A Chemistry 2018, DOI: 10.1016/j.jphotochem.2018.10.052
- 2) Jayaweera, S., Ke, Y. and Ng, W. J. Nitrogen-doped durian shell derived carbon dots for inner filter effect mediated sensing of Tetracycline and fluorescent ink, Journal of fluorescence 2018, DOI: 10.1007/s10895-018-2331-3
- 3) Jayaweera, S., Ke, Y., Hu, X. and Ng, W. J. Fluorescent N/Al co-doped carbon dots from cellulose biomass for sensitive detection of Manganese (VII), Journal of fluorescence 2019, DOI: 10.1007/s10895-019-02452-7

Conference Abstracts

- 1) Jayaweera, S., Ke, Y., Hu, X. and Ng, W. Green Preparation of nitrogen doped carbon nanodots from durian shell waste for the detection of amoxicillin, International Functional Nanomaterials and Nanodevice Conference 2018
- 2) Jayaweera, S., Ke, Y., Hu, X. and Ng, W. J. Green Preparation of Fluorescent Carbon dots from Durian shell waste for highly sensitive detection of Fe^{3+} ions, E2S2-CREATE and AIChE Waste Management Conference 2019