UNIVERSITI PUTRA MALAYSIA

NITROGEN-DOPED CARBON DOTS FROM EMPTY FRUIT BUNCH CARBOXYMETHYLCELLULOSE FOR SELECTIVE DETECTION OF COPPER IONS IN AQUEOUS MEDIA

MOHAMMED ABDULLAH ISSA AL-BADRI

FK 2020 22

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By

MOHAMMED ABDULLAH ISSA AL-BADRI

Thesis Submitted to the School of Graduate Studies, University Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

December 2019

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DEDICATION

To
My lovely parents, Abdullah Issa and Siham Hadi

My beautiful sisters, Hiba and Ghasak

and

My kind friend (Shahad Hadi).

Without Your Support and Encouragement, My Success Wouldn't Have Been Possible.

I am forever in their debt.

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of philosophy

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December 2019

Chairman: Associate Professor Zurina Zainal Abidin, PhD
Faculty: Engineering

Fluorescent carbon dots (CDs) have emerged as sensing systems for wastewater treatment and chemical sensing. Nowadays, different biomass-based materials, including the usage of starch, glucose, and cellulose have been widely employed for the production of CDs. In spite of their sustainability, the fluorescent efficiency of the obtained CDs from these natural resources is still low. This motivates the researchers for doping CDs with various heteroatom species such as nitrogen doping agent. However, long-time synthesis process from 7-72 hr is normally required for obtaining a relatively low fluorescence quantum yield (QY). Additionally, a clear formation mechanism for nitrogen-doped CDs (N-CDs) synthesized hydrothermally from biomass and various heteroatom doping sources along with the origin of the photoluminescence (PL) emission are still under debate.

In this work, one-step hydrothermal carbonization route has been used to produce N-CDs from carboxymethylcellulose (CMC) of oil palms empty fruit bunch in the presence of ethylenediamine (EDA-CDs) and linear-structured polyethyleneimine (LPEI-CDs) in an attempt to enhance the fluorescence quantum yield of CDs. At first, the optimum conditions for the hydrothermal route of N-CDs were identified by assessing the effect of different influential variables (reaction temperature, time, and N-weight). The statistical analysis results indicated that the production of LPEI-CDs not only was obtained in a considerably shorter time in comparison to EDA-CDs but also, they had significantly better fluorescent QY. Additionally, the characterization tests were carried out on the optimum N-CDs. The prepared N-CDs are reproducible, highly homogeneous and excellent PL properties with narrow emission bands. Furthermore, the N-CDs are nearly small (approx. 3-8 nm) with narrow size distributions; are stable over a long period of time (at least six months), and maintain their PL properties when re-dispersed in solution. Moreover, LPEI-CDs showed predominantly crystalline nature, and the functional groups from the LPEI have successfully tuned the PL properties of CDs in both the intrinsic and surface electronic structures, and hence improve the fluorescence

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QY up to 44%. It was concluded that the origin of light emission in N-CDs caused by the interplay between intrinsic state emission originates from graphitic core and extrinsic state emission due to the surface functional groups.

Due to the significant interaction between Cu (II) and amino functional groups over the LPEI-CDs surface, the LPEI-CDs were further used as a fluorescent probe for the detection of Cu (II) in aqueous media. The linear relationship between the relative quenching rate and the concentration of Cu (II) (1–30 μM) with a detection limit of 0.93 μM were used. Considering the sustainable production of N-CDs, this PhD research project provides a guide for converting low-quality waste into value-added nanomaterials and applying for different functionalization processes and analytical applications.

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Abstrak tesis yang dikemukan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

TITIK KARBON BERDOP NITROGEN MENGGUNAKAN KARBOKSIMETIL SELULOSA DARI TANDAN KOSONG KELAPA SAWIT UNTUK MENGESAN KUPRUM SECARA SELEKTIF DALAM MEDIA AKUEUS

Oleh

MOHAMMED ABDULLAH ISSA

Dicember 2019

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Pendafluor titik carbon (CD) telah muncul sebagai sistem pengesanan untuk rawatan air dan pengesanan bahan kimia. Kini, pelbagai bahan yang berasaskan biomas, termasuk penggunaan kanji, glukosa dan selulosa telah digunakan secara meluas dalam pengeluaran CD. Walaupun CD merupakan bahan mampan, namun hasil pendafluor CD yang diperoleh daripada sumber semula jadi ini masih rendah. Hal ini mendorong para penyelidik untuk membuat pengedopan CD dengan pelbagai spesis heteroatom seperti agen pengedopan nitrogen. Walau bagaimanapun, proses sintesis yang panjang dari 7 hingga 72 jam biasanya diperlukan untuk menghasilkan kuantum pendarfluor yang agak rendah (QY). Tambahan pula, mekanisme pembentukan nitrogen berdop CD (N-CDs) secara hidrotermal dari biomas dan pelbagai sumber pengedopan heteroatom serta asal-usul fotoluminesen (PL) masih diperdebatkan.

Dalam kajian ini, kaedah karbonisasi hidrotermal telah digunakan untuk menghasilkan EDA-CDs dan LPEI-CD dari karboksimetil selulosa (CMC) tandan kosong kelapa sawit dengan kehadiran etilinadiamina dan polietilinaimina berstruktur linear dalam usaha untuk meningkatkan penghasilan kuantum pendafluor (QY) CD. Sebagai permulaan, kondisi optimum untuk penghasilan N-CD melalui kaedah hidrotermal N-CD telah dikenalpasti dengan mengkaji pengaruh pembolehubah yang berbeza (suhu tindakbalas, masa, dan berat N). Hasil analisis statistik telah menunjukkan penghasilan LPEI-CD bukan sahaja boleh didapati dalam masa yang lebih singkat berbanding EDA-CD, malah mereka mempunyai pendafluor QY yang jauh lebih baik. Di samping itu, ujian pencirian telah dilaksanakan keatas N-CD yang dihasilkan pada kondisi optimum. N-CD yang terhasil mempamerkan sifat PL yang sangat baik seperti boleh dihasilkan semula, tinggi homogen dan pelepasan jalur yang sempit. Selain itu, N-CD adalah bersaiz kecil (anggaran 3-8 nm) dengan pengagihan saiz yang kecil; stabil dalam jangka masa yang panjang (sekurang-kurangnya enam bulan); dan mengekalkan sifat PL apabila disebarkan semula dalam larutan. Tambahan pula, LPEI-CD telah menunjukkan ciri-ciri kristal yang tinggi dan kumpulan berfungsi dari LPEI telah berjaya menyamai sifat PL

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CD di dalam struktur intrinsik dan permukaan elektronik dan akhirnya meningkatkan pendafluor QY sehingga 44%. Dapat diisimpulkan bahawa asal-usul pelepasan cahaya dalam N-CD adalah disebabkan oleh interaksi antara keadaan pelepasan intrinsik yang berasal dari teras grafitik serta keadaan pelepasan ekstrinsik yang disebabkan oleh kumpulan berfungsi di permukaan.

Oleh kerana interaksi yang baik diantara Cu (II) dengan kumpulan berfungsi amino di permukaan LPEI-CDs, maka LPEI-CDs telah digunakan sebagai prob pendafluor untuk mengesan Cu^{2+} dalam media akueus. Perkaitanan linear di antara kadar relatif pelindapan dan kepekatan Cu^{2+} (antara 1-30 μM) dengan had pengesanan pada 0.93 μM telah digunakan. Dengan mengambilkira penghasilan N-CD yang mampan, projek penyelidikan PhD ini menyediakan panduan untuk menukar sisa yang berkualiti rendah kepada bahan nanomaterial dengan nilai tambah dan menggunakannya untuk pelbagai proses fungsian serta aplikasi analisis.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
AIE	Aggregation Induced Emission
ANOVA	Analysis of Variance
ASV	Anodic Stripping Voltammetry
BBD	Box-Behnken Design
BPEI	Branched Polyethyleneimine
CDs	Carbon Dots
CCD	Central Composite Design
CEE	Crosslink-Enhanced Emission
CMC	Carboxymethylcellulose
CNDs	Carbon Nanodots
CV	Coefficient of Variation
CQDs	Carbon Quantum Dots
$CuNO_3$	Copper Nitrate
DFT	Density Functional Theory
DI	Deionized Water
DLS	Dynamic Light Scattering
EDA	Ethylenediamine
EDA-CDs	Ethylenediamine Derived Carbon Dots
EDC	1-ethyl-3-(3- dimethylaminopropyl) carbodiimide
EDTA	Ethylenediaminetetraacetic acid
EFB	Empty Fruit Bunch
EPA	Environmental Protection Agency
F-CCD	Face-Centered Central Composite Design
FTIR	Fourier Transform Infrared
FWHM	Full Width at Half Maximum
GCQDs	Graphene Carbon Quantum Dots
Ge	Germanium
GFP	Green Fluorescent Protein
GO	Graphene Oxide
HMF	Hydroxymethylfurfural
HNO_3	Nitric Acid
HOMO	Highest Occupied Molecular Orbital
HRTEM	High-Resolution Transmission Electron Microscopy
HTC	Hydrothermal Carbonization Route
ICPMS	Inductively Coupled Plasma Mass Spectrometry
IFE	Isolated Fluorophore Effect
IC	Internal Conversion
ICT	Internal Charge-Transfer
ISC	Intersystem Crossing
INAA	Instrumental Neutron Activation Analysis
LBL	Layer-by-Layer
LED	Light-Emitting Diode
LOD	Limit of Detection

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LPEI	Linear-Structured Polyethyleneimine
LPEI-CDs	Linear- Structured Polyethyleneimine derived Carbon Dots
LUMO	Lowest Unoccupied Molecular Orbital
MLS	Method of Least Square
MSS	Mercaptosuccinic Acid
MWCNT	Multiwalled Carbon Nanotubes
NA	Number of Absorbed Photons
NE	Number of Emitted Photons
N-CDs	Nitrogen-doped Carbon Dots
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide
NHS	N-hydroxy-Succinimide
OD	Optical Density
PDs	Polymer Dots
PEG	Polyethylene Glycol
PGP	Peach Gum Polysaccharide
PL	Photoluminescence
PPEI-EI	Poly (propionyl ethyleneimine-co- ethyleneimine)
PRESS	Predicted Error Sum of Squares
PVL	Poly (Vinyl Alcohol)
QCE	Quantum Confinement Effect
QDs	Quantum Dots
QY	Quantum Yield
RSM	Response Surface Methodology
SCWE	Subcritical Water Extraction
Sidots	Silicon Dots
TEM	Transmission Electron Microscopy
TDDFT	Time-Dependent Density Functional Theory
UV-VIS	Ultraviolet-Visible Spectroscopy
WHO	World Health Organization
XRF	X-ray Fluorescence Spectrometry
XPS	X-ray Photoelectron Spectroscopy
3D	Three-Dimensional
Λem	Emission Wavelength
Λex	Excitation Wavelength

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CHAPTER 1

INTRODUCTION

1.1 Background

Carbon dots (CDs), a new member of fluorescent carbon nanostructures family, with sizes of less than 10 nm, have drawn considerable attention among researchers since their first fundamental report (Sun et al., 2006). CDs consist of graphitic or amorphous carbon core coated with oxygen-functionalities, polymers and other active groups with respect to synthesis condition and surface chemistry (Liu et al., 2017). Compared to traditional semiconductor quantum dots (QDs) and organic dyes, carbon dots have outstanding properties such as good biocompatibility, tuneable photoluminescence, chemical inertness and ease of production (Li & Dong, 2018; Ren et al., 2017; Sun & Lei, 2017).

Many methods, including arc-discharge approach (Xu et al., 2004), Electrochemical oxidation (Li et al., 2010), microwave treatment (Purbia & Paria, 2016) and hydrothermal carbonization approach (Sahu et al., 2012), have been recently established. Although a large diversity of techniques and carbonaceous precursors were used for the production of CDs, these techniques generally require costly equipment and harsh toxic chemicals. One way to reduce overall preparation costs is the use of biological waste as starting material. Hence, natural and renewable resources such as grass (Qin et al., 2013), glucose (Dou et al., 2015), date palm frond (Kavitha & Kumar, 2018) and cellulose (Shen et al., 2016; Wu et al., 2015) have been used for the preparation of CDs. However, the fluorescence QY of the formed CDs are less than 10%, restricting their practical applications. To address these issues, much work has been reported to enhance the electronic characteristics of CDs, including doping with nonmetal heteroatoms (like nitrogen, boron and silver) as they significantly improve the fluorescence efficiency, increase the resistance to photo-bleaching and sensing selectivity to different analytes (Liao et al., 2016).

In particular, N- doping source, also known as an electron donator, has been shown to be the most convenient element on the stimulating of electronic states of the carbonaceous material by introducing new energy states corresponding to the N- dopants (Li & Dong, 2018). In contrast to the undoped CDs, N-CDs becomes optically active, showing obvious PL from visible to near-infrared spectral regions (Li & Dong, 2018). Thus, the PL properties of N-CDs can be tuned through controlling the particle size, choice of dopant, influence of the passivating species, pH, time, temperature, nature of the solvent, and so on. In spite of high achievements have been made in the development of N-CDs, some problems such as PL origin, and the corresponding interaction variables in production are still controversial and need to be further discussed.

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Water pollution by metal ions released by anthropogenic activities has become a worldwide issue owing to their severe threats to human health and environment (Gumpu et al., 2015; Kumar et al., 2017). Therefore, in the past few decades, various conventional methods have been employed for the determination of heavy metals in aqueous solution include, atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICPMS), anodic stripping voltammetry (ASV), X-ray fluorescence spectrometry (XRF), instrumental neutron activation analysis (INAA) (Bansod et al., 2017; Guo et al., 2015; Li et al., 2013). Although these techniques are highly sensitive, specific and precise, they show some shortcomings including high expense, lack of portability, the need for complex operational procedures, and long detection times. More recently, QDs have drawn much attention for fluorescent sensing of metal ions (Yu et al., 2015), owing to their good optical characteristics and biocompatibility. However, several problems have arisen from their inherent toxicity owing to their intrinsically metal-based elements. Thus, it is essential to develop a simple method for synthesis of cheap and biocompatible nanomaterials.

Due to the non-toxic carbon core and existing hydrophilic groups which act as the receptors, to react with the metal ions causing the change of signals subsequently, CDs are possible to be applied as fluorescence probes. To date, CDs sensitivity to varieties of ions, including ferric ions (Zhu et al., 2013b; Edison et al., 2016), lead ions (Wee et al., 2013), mercury ions , copper ions (Liu et al., 2012; Ma et al., 2017; Singh et al., 2017; Zong et al., 2014), and many others, have been developed to enhance the performance of optical sensing systems in terms of sensitivity, detection limit, selectivity, and biocompatibility. Therefore, given the aforementioned advantages of CDs for metal ions sensing, finding highly fluorescent QY of CDs and as well as understanding and identifying the optical and chemical composition of the prepared CDs from sustainable bioresources in the presence of various N- additives are vitally important.

1.2 Problem Statement

1.2.1 Why New Detection Method is Needed?

Copper is one of the essential transition metal ions in the human body. Cu^{2+} is necessary for significant physiological functions, but the excessive dose of Cu^{2+} in the body can cause adverse impact, including Menkes, Prion, Wilsons and Alzheimer's diseases (Singh et al., 2017). Moreover, copper is highly exploited by industries, environment, and domestic functions. Due to this danger, the fundamental toxicity guidelines for heavy metals in drinking water have been established, in which the permissible limits of copper ions in drinking water were settled to be 2 and 1.3 mg/l as recommended by the World Health Organization (WHO) and Environmental Protection Agency (EPA), respectively (Pawan et al., 1990). Therefore, finding a safe method for monitoring these toxic metals, especially in water, with selective and sensitive detection of Cu^{2+} is highly desirable.

Compared to the traditional techniques that have been developed for the determination of Cu^{2+} (Basabe-Desmonts et al., 2007; Yang et al., 2016), fluorescent nanomaterials can

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improve the performance of sensing systems in terms of selectivity and sensitivity with less sophisticated process. Over the last few decades, nanomaterials- based strategies have gained high interest for biological monitoring, chemical sensing and others. Among them, novel metal-based nanomaterials, such as Au, Ag have been usually used for selective detection with electrochemical techniques and fluorescence measurements (Zhang et al., 2013). However, metal nanoparticle-electrochemical combined strategies require multiple steps, including extensive pre-treatments of the electrode surface (polishing, surface contamination oxidation, and others), which cannot be easily automated and thus affects their application as ideal systems. Meanwhile, to decrease the cost of the sensors fabricated from noble metals, it is necessary to develop low-cost materials-based chemosensors.

Because of the high emission quantum yield and size-tunable emission profiles, semiconductor quantum dots (QDs), such as CdSe and CdTe, have become one of the most extensively investigated optical sensing nanomaterials in the detection of metal ions. For instance, CdSe QDs with a low detection limit of 5 nm was demonstrated for the determination of Cu (II) (Chan et al., 2010). However, these fluorescent QDs are limited due to the fact that they are toxic, low sensitive, low selective, hydrophobic or costly (Ren et al., 2017). In addition, their superior photophysical features are usually observed in organic solvents, thus restricting tremendously their analytical potential (Zeng et al., 2015). Compared to the traditional QDs, fluorescent CDs can be used as strong competitors and potential alternatives to that heavy metal-based owing to their low to non-toxicity (Kong et al., 2015). In other words, CDs are one type of QDs, but the core of CDs is made up of carbon rather than metallic complex, making them suitable for sensing of various analytes and for biological analysis.

1.2.2 Why Carboxymethylcellulose from Empty Fruit Bunch?

To synthesize CDs, the selection of a suitable starting material plays a significant role. A perfect carbon source for green CD synthesis should be accessible worldwide with defined and well-known properties, should not be in direct competition with essential food production, and last but not least, be cost-effective (Lim et al., 2014; Prat et al., 2014). While the price of additives or carbon sources plays a minor role in fundamental research, it may play a major role when commercial quantities are considered. With the aim of producing biocompatible CDs, it has been proposed to use a biologically safe compound as starting precursor. Cellulose, for instance, is a polysaccharide that is abundant in nature and easily extractable from biomass waste. The broad usage of cellulose as supercapacitors, catalyst supports, and adsorbents has rendered it safe for consumption and therefore can minimize the toxicity risk (Brinchi et al., 2013; Souza et al., 2016).

Palm oil industry has contributed significantly to Malaysia economy. However, lignocellulosic biomass specifically empty fruit bunch, which contributes 22% of total wastage from the palm oil extractions, has created a major disposal problem (Abdullah & Sulaiman, 2013). Therefore, by taking these considerations, this study attempts to convert empty fruit bunch into more valuable materials which are in the

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form of CMC, where the utilization of these undesirable wastes is a clear advantage in terms of environmental impact.

Since CMC does not contain N-functionalities in its structure, obtaining superior fluorescent properties of these high abundances and renewable sources is the critical step. Thus, in order to exploit CMC as the starting material, further improvement of PL properties using N-doping strategy is quite essential. Recently, the usage of CMC has been employed as precursor in the presence of N- additives for the production of N-CDs. For instance, Q. Wu et al., (2015) synthesized N-CDs from CMC (source in not specified) in the presence of urea as the nitrogen source. The obtained blue-green aqueous N-CDs with an average diameter of 32 nm and QY of 18% show excitation- and emission-independent pH-sensitive properties (Wu et al., 2015). Additionally, fluorescent N-CDs with a QY of 21% were obtained via hydrothermal treatment of cellulose (the specific type is not defined in the original report) in the presence of urea (Shen et al., 2016). In another study, Wang et al., (2017) synthesized a blue-color N-CDs from cellulose in the presence of ammonium carbonate. The obtained N-CDs are mainly spherical morphology with an average diameter of 1.5 nm and QY of 7.6%. Generally, the QY of CDs is low (<10%), whereas the QY can be increased to 10-30% (a few examples even reach as high as 50–80%) after surface passivation. However, the needs to find alternative agents which can play an effective role to manipulate the intrinsic properties and improve the optical performances of CDs, and even produce unexpected phenomena and applications is highly desirable.

1.2.3 Why Short-time Hydrothermal Route is Significant?

For the synthesis part, top-down approach which involves physical changes to the starting material often requires costly and complicated instrumental setup. Therefore, the bottom-up method is more favorable as the simple and facile synthetic routes can be carried out easily in laboratory without elaborated experimental conditions. Hydrothermal carbonization route (HTC) is a promising synthesis route, which is fast, economical, and eco-friendly in comparison with other synthesis methods (Falco et al., 2011; Shen et al., 2018).

Since the obtained QY is highly dependent on the starting materials and synthesis conditions used, the ease of theprocessing and no need for high temperature and long-time synthesis process is of great interest. Hence, efforts have to be made to avoid today's scenario observed for QDs. While having amazing properties and interesting uses, they still have not achieved their full potential in commercial applications due to significant production costs, low fluorescence efficiency and long-time synthesis process (Derfus et al., 2004; Wang et al., 2013). For instance, Shen et al., (2016) synthesized N-CDs from cellulose and urea as carbon and nitrogen sources, respectively through HTC process. In their study, QY of 21% was obtained and the time consumed is 72 hr. In another study, N-CDs obtained from hydrothermal treatment of cellulose and ammonium carbonate, in which 12 hr of synthesis time was found to be sufficient for the carbonization conversion rate and obtaining QY of 7.6% (Wang et al., 2017). Similar findings were also reported (Dou et al., 2015; Li et al., 2010; Wu et al., 2017; Wu et al.,

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2015), in which low QY and/or long synthesis time needed for the production of CDs using biomass as a sole precursors or even after doping them with various N- additives.

1.2.4 Knowledge Gap in Current Studies

As previously mentioned, the ease of the processing and no need for high temperature and long-time synthesis process can be quite useful for the industry. Additionally, the investigation into the effect of the synthesis parameters such as temperature, time, and N- additive would be very beneficial for evaluating the fluorescence efficiency of the obtained N-CDs. Yet, to the best of our knowledge, so far, no study on the preparation of N-CDs from CMC of empty fruit bunch has been carried out. Additionally, the study on the combination interaction between the influential conditions and the QY using hydrothermal route is very limited (only one study exists: Barati et al., (2015). Hence, more investigation on the N-CDs of CMC is needed.

Previous research related to the comparative analysis of the physicochemical properties using various N- additives are rarely studied. Under identical conditions, Sachdev et al., (2014) evaluated the optical performance of polyethylene glycol (PEG) and polyethyleneimine (PEI) on the hydrothermal carbonization of chitosan. Various QYs, structures and chemical properties of the obtained N-CDs were resulted using different N- additives. However, a clear formation mechanism for nitrogen-doped CDs (N-CDs) synthesized from saccharides and various heteroatom doping sources along with the origin of the PL emission are still under debate.

Furthermore, the usage of lignocellulosic waste has been recently documented for the production of N-CDs, in which various QYs using different synthesis conditions were obtained. It is well known that the formation of N-CDs depends on the degree of the substitution of the cellulose structure (i. e. how many of the OH^- have taken part in the substitution reaction), as well as the chain length of the cellulose backbone and the degree of clustering of the cellulose substituents. Most of reported works show several shortcomings including low fluorescence QY and long preparation time (Wu et al., 2015; Shen et al., 2016; Wang et al., 2017). These drawbacks may relate to the absence of ether groups within the cellulose framework and as a results lower substitution reaction could be occurred. CMC of EFB is rich with ether and hydroxyl groups which could play the major role for the successive rearrangement reactions leading to process acceleration. Thus, full exploitation of these biomass waste can be done by maximizing the utilization of these resources to form products of high value which not only comply to the zero-waste strategy but also generate additional profit to the palm oil industry. To the best of the knowledge of the current authors, no earlier work has been carried out to synthesis N-CDs from CMC of EFB in the presence of EDA and LPEI as both the carbon source and nitrogen atom/ surface passivation agents, respectively using different synthesis conditions.

The greatest challenges in heavy metal ions detection are the necessity of using short synthesis time for the production of highly fluorescence N-CDs and low sensitivity at the

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same time. Copper ion detection has an association with long-time synthesis process and low QY and this has been established by preview workers (Zhu et al., 2012). Additionally, CDs have been widely applied as a fluorescent probe for the determination of Cu (II) with high selectivity and sensitivity. However, several drawbacks limit their metal ions application, including long response time of more than 10 min (Liu et al., 2012; Ma et al., 2017; Singh et al., 2017; Zong et al., 2014a), narrow detection interval (Ma et al., 2017; Salinas-Castillo et al., 2013; Salinas-castillo et al., 2016), high detection limit (Ganiga & Cyriac, 2016; Ma et al., 2017; Wen et al., 2014; Zong et al., 2014), or complex probe synthesis (Liu et al., 2012; Salinas-Castillo et al., 2013; Zong et al., 2014). Therefore, it would be sensible to develop highly fluorescent N-CDs in significantly short synthesis time as well as to improve the detection sensitivity of copper ions in aqueous media.

1.3 Significance of the Study/ Practical Contribution

The main contribution of the study comprises:

i. By using EFB CMC as the main carbon source for obtaining N-CDs, it is possible to convert low-value materials into useful compounds, where the utilization of these undesirable wastes is a clear advantage in terms of environmental impact.
ii. By incorporating LPEI into the final structure of carbon particles, this study can take a big step in providing useful information for the N-CDs formation and/or emission mechanism and exploiting these sustainable fluorescent nanomaterials for further functionalization and analytical applications.
iii. By optimizing the hydrothermal synthesis process of N-CDs using CCD-RSM, this step can be quite beneficial, where shorter reaction times and lower temperatures are more favored during the hydrothermal treatment and consequently reduce the cost and money.

1.4 Objectives of the Study

The goal of this study is to develop fluorescent carbon dots from sustainable and cost-effective natural resources as optical sensing receptor for detection of copper ions in water. The following specific objectives were designed to achieve this goal;

i. To optimize one-pot hydrothermal route for the synthesis of N-CDs from CMC of oil palm empty fruit bunch (EFB) incorporated with EDA and LPEI as N- additives.
ii. To characterize the numerically optimized EDA-CDs and LPEI-CDs.
iii. To investigate the fluorescence stability of the optimized LPEI-CDs.
iv. To evaluate the potential applications of the optimized LPEI-CDs on detection of Cu^{+2} in aqueous solutions using Stern-Volmer quenching analysis.

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1.5 Research Hypothesis

The present study attempts to synthesize and analyze N-CDs from EFB CMC using HTC approach which could provide a foundation to identify the chemical composition of a probe. This fluorescent probe can be used to obtain a selective response to heavy metal ions that will cause a measurable change of optical properties of N-CDs. The usage of CMC for the production of N-CDs is believed to have a higher degree of substitution than other lignocellulosic waste due to the abundant of hydroxyl and ether moieties within CMC structure. In other words, higher aromatization reaction could be occurred as a result of rapid clustering degree and rearrangement of the CMC substituents, leading to the formation of N-CDs in considerably milder synthesis conditions.

In sensor applications, the low detection limit and selectivity are depending directly on the sensing precursors and the detection process. Thus, that fluorescent probe doping with nitrogen agent can play a vital role in detection. The existence of N- species can provide more active sites over the surface of N-CDs, leading to higher binding affinity to interact with metal ions compared to the undoped ones.

1.6 Scope of Research

In this research study, the focus is to synthesize fluorescent nitrogen-doped carbon dots (N-CDs) from renewable resources and exploit the prepared N-CDs in the enhancement performance of selective detection of heavy metal ions using N-CDs as a chemical sensor.

i. Response surface methodology (RSM) was used to design the synthesis experiments by hydrothermal carbonization method from CMC of EFB with the incorporation of two doping agents mainly EDA and LPEI. A central composite design was used to optimize operational parameters of the synthesis of N-CDs by hydrothermal carbonization route.
ii. The optimization of hydrothermal carbonization method was assessed based on the fluorescence quantum yield (QY) of the synthesized N-CDs at different temperature, reaction time, and doping weight. The QY of all the experimental runs that suggested by Design Experts software were calculated based on the comparative method using quinine sulfate as a reference, where both of the absorption and fluorescence spectra were analyzed.
iii. The numerically optimized aqueous solution of hydrothermal process in synthesis of N-CDs was assessed based on the results of TEM, HRTEM, FTIR, XPS, UV-VIS, PL spectroscopy, and zeta potential.
iv. The formed N-CDs obtained in the presence of LPEI doping agent were selected for the subsequent experiments due to their highest obtained QY.
v. The photostability properties of the optimized N-CDs were evaluated by identifying the influence of N-CDs concentration, pH, time of exposure, storage time and ionic strength on the PL stability of N-CDs.

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vi. Sensor performance were achieved by evaluating the selectivity study through measuring the PL spectra of N-CDs in the absence and presence of different metal cations, including Fe (III), Fe (II), Pb (II), Cu (II), Mg (II), Ca (II), Cd (II), Zn (II), Hg (II) and Mn (II) ions.

vii. The sensitivity study of the fluorescent sensor was evaluated by measuring the PL spectra of N-CDs in the absence and presence of different receptor concentrations and hence the limit of detection was analyzed.

1.7 Thesis Structure

This thesis is divided into five chapters. Chapter one covers introduction, problem statements, objectives, scope and thesis structure. Chapter two includes descriptions on the fluorescent carbon dots, including their benefits, fabrication methods, starting materials used and fluorescent enhancement using various surface passivation and /or doping agents. The main structure of CMC and their advantages for exploiting them as potential starting precursors were explained. Also, an introduction to the various characterization measurements used throughout the study was explained and the principle of fluorescence was clarified. Furthermore, sensing applications, including theory of fluorescence quenching, possible mechanisms, sensor design, and immobilization/embedment techniques were thoroughly explained. Moreover, the theory of multi-objective design optimization using response surface methodology was explained shortly. In chapter three, both the materials and method for producing N-CDs from CMC in the presence of EDA and LPEI are elaborated. Moreover, the characterization methods (TEM, HRTEM, FTIR, XPS, UV-Vis, and PL spectra) for testing the obtained EDA-CDs and LPEI-CDs were explained. The method of fluorescence stability in terms of N-CDs concentration, pH, surface charge, irradiation time, storage time and ionic strength on the fluorescence of N-CDs was discussed. Finally, the methodology of using N-CDs as a selective and sensitive probe for Cu^{2+} sensing as well as the analysis of real samples was explained. In chapter four, the results of experiments were thoroughly explained and discussed. Chapter four consists preparation of N-CDs from CMC using EDA and LPEI, including QY calculation, study the effect of key parameters. An experimental design using Central Composite Design (CCD) was done on the production of N-CDs from CMC in the presence of EDA and LPEI. Then it continues to optimize operational variables using RSM. The results of several characterization tests of both numerically optimized EDA-CDs and LPEI-CDs were analyzed and investigated. Based on the characterization tests, a detailed fluorescence origin and potential formation mechanism of N-CDs were systematically elaborated. The results of photostability measurements were explained. The feasibility of N-CDs-based-Cu^{2+} sensor, as well as the possible sensing mechanism, were discussed. Finally, the overview of the study, conclusion, and the direction for future studies were presented in Chapter 5.

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This thesis has been conducted by Mohammed Abdullah who was born on 19th February 1989 in Iraq. In 2010, he received his bachelor degree in environmental engineering at University of Al-Mustansiriya. He got his master degree in Environmental Technology and Management from UPM University Putra Malaysia in 2016, under supervision of Associate Prof. Dr. Zurina Zainal Abidin. His research focused on Plant-based coagulants and its effect for removing turbidity from wastewater. In 2016, he started his Ph.D. At Environmental Engineering under similar supervision. His research focuses on the production of fluorescent carbon dots from sustainable materials for sensing heavy metals and design new sensing layer for the enhancement of optical sensors.

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