UNIVERSITI PUTRA MALAYSIA

FACILE PREPARATION OF CARBON QUANTUM DOTS FROM BIOCHAR VIA MICROWAVE–ASSISTED HYDROTHERMAL SYNTHESIS

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By

ALIF SYAFIQ BIN KAMAROL ZAMAN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

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FACILE PREPARATION OF CARBON QUANTUM DOTS FROM BIOCHAR VIA MICROWAVE–ASSISTED HYDROTHERMAL

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August 2019

Chairman : Suraya Abdul Rashid, PhD
Faculty : Institute of Advanced Technology

Carbon quantum dots (CQD) were successfully synthesized using microwave-assisted hydrothermal method using empty fruit bunch (EFB) biochar as the carbon precursor. Effect of temperature (60°C – 130°C), solvent concentration (0.1- 0.5 mole fraction of IPA) and reaction time (5 – 30 minutes) were investigated on CQD yield (%). The optimum process gives the highest yield and it is about 15.22% at 100°C with 0.1 mole fraction and in just 5 minutes. Material characterisations confirm the formation of CQD where microscopy images showed an average size distribution of 4.5 nm. Chemical structure has shown the presence of oxygenic functional groups such as hydroxyl, carbonyl/carboxyl at 3270 cm^{-1} and 1640 cm^{-1} respectively. The presence of these oxygenic functional groups are also supported by X-ray Photoelectron Spectroscopy analysis where C–C/C=C (284.6 eV), C-O (285.5 eV), C=O (286.5 eV) and COOH (288.1 eV). To complement experimental data, density functional theory (DFT) calculations were carried out at 6-31G(d) basis set and a comparison of three exchange correlation functions such as B3LYP, CAM-B3LYP and wB97XD. These functionals are able to calculate the ground state molecular structure of CQD where the subsequent frequency analyses for each functionals give no imaginary frequencies. The highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO-LUMO) gap obtained from 6–31G(d) with Becke's three parameter with Lee–Yang–Parr (B3LYP) is 6.381 eV and is closer to experimental band gap of 3.2 eV compared to Coulomb attenuating method with Becke's three parameter with Lee–Yang–Parr (CAM–B3LYP) and wB97XD. In conclusion, a facile preparation of CQD from EFB biochar was successfully obtained from microwave-assisted hydrothermal process. The process was efficient, rapid, cost-effective and eco-friendly.

Abstrak thesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Sains Master

PENYEDIAAN MUDAH TITIK KARBON KUANTUM MENGGUNAKAN BANTUAN SINTESIS GELOMBANG MIKRO HIDROTERMA

Oleh

ALIF SYAFIQ BIN KAMAROL ZAMAN

Ogos 2019

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Titik karbon kuantum (CQD) telah berjaya disintesis dengan menggunakan kaedah bantuan gelombang mikro hidroterma menggunakan tandan buah kosong (EFB) arang bio sebagai bentuk awal karbon. Kesan suhu (60°C–130°C), kepekatan pelarut (0.1–0.5 pecahan mol IPA) dan masa tindak balas (5–30 minit) disiasat pada hasil CQD (%). Proses optimal memberikan hasil tertinggi dan kira-kira 15.22% pada 100°C dengan 0.1 pecahan mol dan hanya dalam 5 minit. Ciri-ciri bahan mengesahkan pembentukan CQD di mana imej mikroskopi menunjukkan pengedaran saiz purata 4.5 nm.Struktur kimia telah menunjukkan kehadiran kumpulan berfungsi oksigen seperti hidroksil, karbonil / karboksil masing-masing pada 3270 cm^{-1} dan 1640 cm^{-1}. Kehadiran kumpulan fungsi oksigen ini juga disokong oleh analisis X-ray Photoelectron Spectroscopy di mana C–C / C=C (284.6 eV), CO (285.5 eV), C=O (286.5 eV) dan COOH (288.1 eV). Untuk melengkapi data eksperimen, pengiraan teori fungsi kepadatan (DFT) dilakukan pada set asas 6-31G (d) dan perbandingan tiga fungsi korelasi pertukaran seperti B3LYP, CAM-B3LYP dan wB97XD. Fungsi-fungsi ini dapat menghitung keadaan dasar struktur molekul CQD di mana analisis kekerapan berikutnya untuk setiap fungsi tidak memberikan frekuensi khayalan. Jurang orbital molekul tertinggi yang dipenuhi dan orbital molekul terendah yang tidak dipenuhi (HOMO-LUMO) yang diperoleh dari 6-31G (d) dengan tiga parameter Becke dengan Lee–Yang–Parr (B3LYP) adalah 6.381 eV dan ia adalah lebih dekat dengan jurang band eksperimen iaitu sebanyak 3.2 eV berbanding kaedah pelepasan Coulomb dengan tiga parameter Becke dengan Lee–Yang–Parr (CAM-B3LYP) dan wB97XD. Kesimpulannya, penyediaan CQD dari arang bio menggunakan tandan buah kosong (EFB) berjaya diperoleh daripada proses gelombang mikro hidrotermal. Proses tersebut merupakan proses yang cekap, cepat, kos efektif dan mesra alam.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

CAM-B3LYP	Coulomb attenuating method–Becke's three parameter with Lee–Yang–Parr non local electron correlation
CdSe	Cadmium Selenide
CO_2	Carbon dioxide
CQD	Carbon quantum dots
EFB	Empty fruit bunch
FTIR	Fourier Transform Infrared
HOMO	Highest occupied molecular orbital
HR–TEM	High resolution transmission electron microscope
IEFPCM	Integral equation formalism polarizable continuum model
IPA	Isopropanol
LSDA	Local-spin density approximation
LUMO	Lowest unoccupied molecular orbital
MESP	Molecular electrostatic surface potential map
NIR	Near infrared
PL	Photoluminescence
QCE	Quantum confinement effect
SAED	Selected area electron diffraction
UV	Ultraviolet-light
VLE	Vapour-liquid equilibrium
XPS	X-ray photoelectron spectroscopy
ZnS	Zinc Sulphide
ZnSe	Zinc Selenide

CHAPTER 1

INTRODUCTION

1.1 Background Study

Quantum dots (QD) have long since piqued interest in scientists since its discovery because of their wide range of applications in many field of science due to its tuneable bandgap and high surface to volume ratio (Shin et al., 2014). Essentially, QD is a nanomaterial typically ranging from 2 nm to 10 nm in size (Sun et al., 2013). Being zero-dimensional nanostructures, they exhibit a very unique property which is photoluminescence and to make it more interesting, the colour of photoluminescence exhibited depends on its size. The smaller the size of the QD, the shorter the wavelength and will emit blue colour emission when excited under ultraviolet (UV) light. Most of synthesized QD are derived from metal precursors such as Cadmium Selenide (CdSe), Zinc Sulphide (ZnS), Zinc Selenide (ZnSe) for light-harvesting application, quick detection and process of energy transfer (Chandra et al., 2014). However, as the application trend of metal QD evolve, it is well-known that metal QD have higher toxicity because most of them are transition metal derived QD (Xiao et al., 2016). To tackle this issue, scientists have come up with an alternative precursor to produce QD—ideally carbon due to its abundance.

Therefore, QD produced from carbon precursors is called carbon quantum dots and will be referred as CQD. CQD have excellent properties comparable to its metal QD counterparts such as low-toxicity, biocompatibility, and good water solubility (Isnaeni et al., 2018; Zheng et al., 2017). The process of producing CQD is generally divided into two types of approaches: top–down and bottom–up. The top–down approach involves from various carbon precursors such as graphite or graphene oxide using modified Hummer's method and hydrothermal route (Pan et al., 2010; Zhu et al., 2011). The bottom–up approach can be regarded as assembling small molecules into bigger molecules such as glucose and citric acid through carbonization process (Cao et al., 2015; Guo et al., 2017). In addition, CQD can be utilized in the fields of medical, environmental and agriculture such as bio-imaging, bio-sensing and photocatalysis.

Empty fruit bunch (EFB) biochar is a type of palm oil tree biomass that is rich in carbon can be used as a better alternative and much more cost-effective carbon source and energy saving for producing CQD. Malaysia is producing the largest amount of palm oil tree biomass and converting them into useful product and further utilization will support global movement to develop sustainable technology and reduce carbon footprint in order to save the planet (Shuit et al., 2009; Thambiraj & Shankaran, 2016). It is also necessary to establish a facile and green process of producing CQD using easily accessible waste (EFB biochar) that is feasible for scaling up. The most suitable heating method for this process is microwave–assisted hydrothermal due its uniform heating and steep temperature gradient. Plus, this heating method can be carried out with larger volume. Microwave–assisted hydrothermal is also considered to be much more efficient compared to other methods due its heat transfer mechanism where it can interact directly with the sample matrix by ionic conductions and dipolar rotation whilst increasing the likelihood of a reaction to occur (Kanitkar et al., 2011). Besides that, obtaining molecular insights on CQD molecule is also important if the properties of CQD is to be analysed.

Density functional theory (DFT), is a very suitable method to predict or simulate some of the properties of CQD.The data obtained from DFT calculations can be compared with experimental data in order to validate whether both data are in agreement with each other. Appropriate choice of basis sets and exchange correlation functions can have a huge impact on the quality of the results (Hill, 2013; Srivastava et al., 2017). Therefore, in this work, a greener alternative, cost-effective and less time consuming process of producing CQD from EFB biochar using microwave assisted process. The characterization will be done on the CQD obtained from the optimum parameters. Lastly, data from DFT calculation will be used to compare and complement the experimental data.

1.2 Problems Statement

Generally, most top-down methods for the synthesis of CQD use chemicals that are toxic to the environment and also require longer reaction time (more than 2 hours) to produce significant yield (Qu et al., 2015; Wang et al., 2011). Hummer's method risks are often underestimated as it because the addition of potassium permanganate and sulphuric acid can cause explosions if not done correctly (Bacon et al., 2014). The reaction time needed also could go up to long hours which can be quite exhaustive. Although using acids can provide higher yields, it is still harmful to the environment and can be difficult to handle. It has also been reported that bottom-up approach where small molecules such as citric acid and glucose have been used to synthesize CQD which possess excellent optical properties and application (Cao et al., 2015; Guo et al., 2017). However, these methods are still costly multi-step processes, harsh synthetic conditions and also time consuming. Yongli Liu *et. al* have synthesized CQD from sodium citrate and polyacrylamide but the reaction time is 3 hours and at 200°C (Liu et al., 2017).

This method is not suitable for scaling up due to expensive starting material, inconvenient production and recovery processes. Previous studies have attempted to use biomass as starting material but the production process still uses solvents that are harmful to the environment (Duan et al., 2016; Pramanik et al., 2018). Hence, a complete exclusion of the dangerous chemicals, cost-effective and low reaction time in developing a green and facile process to produce CQD is the biggest challenge in CQD synthesis methods. To take advantage of the abundance production from oil palm mills in Malaysia, biomass from oil palm empty fruit bunch (EFB) biochar (Zamani et al., 2017) may be use as a starting material for CQD. Biochar is produced by heating the carbon rich material in oxygen deprived conditions (pyrolysis) making it a sustainable method to reduce gases production from global warming (Laird D.A., 2008). Previously, the utilization of EFB into biochar has been used as an alternative sustainable source of soil fertility (Menon et al., 2006).

To date, there is no research on using empty fruit bunch (EFB) biochar as starting material for CQD. Besides that, it is also deemed important to compare experimental results with the results obtained from computer simulations. DFT is one of many computational methods to predict electronic and molecular properties of CQD. Previous DFT works have shown that the prediction of electronic and molecular properties can be accurate and comparable to experimental results by carefully modelling the CQD structure and also the choice of methods (basis sets and exchange correlation functionals). Choosing the appropriate basis set and exchange correlation functionals will be crucial in this study. Furthermore, the presence of functional groups in CQD structure does play affect its electronic and molecular properties. By drawing the appropriate CQD structure, the more accurate the prediction will be.

1.3 Research Objectives

The goal of this research is to develop a green and facile microwave–assisted hydrothermal process for producing CQD using EFB biochar as the carbon precursor and compare the experimental data with the data obtained from DFT calculations. The objectives of this research are:

a) To determine the effects of temperature, solvent concentration and time on the yield of CQD using microwave–assisted hydrothermal process.
b) To investigate the morphological and chemical properties of CQD.
c) To investigate the electronic and molecular properties of CQD using density functional theory.

1.4 Scope of Work

The above mentioned objectives were achieved by carrying out a number of research activities throughout the study period. The scope of work are based on each objectives:

1. **First objective**
    a. Synthesis of carbon quantum dots (CQD) from empty fruit bunch (EFB) biochar *via* microwave–assisted hydrothermal synthesis.
    b. Investigation of the effects of temperature, solvent concentration and time on CQD yield.
2. **Second objective**
    a. Characterisations of CQD using UV-Vis, PL, FTIR, XPS and Raman spectroscopy as well as HR–TEM micrographs for morphology.
    b. Explain the formation mechanism of CQD by incorporating interdisciplinary scientific domains such as material science, physics, chemistry and chemical engineering elements.
3. **Third objective**
    a. Molecular modelling based on Density Functional Theory (DFT) and compare the theoretical results with experimental results.
    b. Determine the most suitable exchange correlation functional from DFT calculation.

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