Microwave-assisted synthesis of photoluminescent carbon dots from palm fronds biomass wastes

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Abstract. Oil palm fronds (OPF) is one of the largest biomass sources in Malaysia that has been underutilized. In this work, OPF has been used as a precursor to synthesize carbon dots (CDs) via microwave irradiation method. The impacts of irradiation power and duration and the reacting solution have been investigated. It was discovered that CDs with the highest photoluminescence intensity was obtained at microwave irradiation power of 385 W for 30 s. Irradiation at lower or higher power resulted in incomplete or over carbonization that reduced the fluorescence property. In addition, CDs synthesized with diethylene glycol (DEG) as reacting solution possessed higher photoluminescence intensity as compared to ultrapure water solution. This could be attributed to more complete CDs formation that happened at higher temperature, which could only be achieved by DEG solution (higher boiling point). The CDs were then tested as a sensor for lead (II) ions. The UV-vis absorbance was found to be reduced with the presence of lead (II) ions. This indicated that the lead (II) ions might interact with CDs and disrupted with the absorbance of UV light. Overall, OPF could be a potential precursor for the synthesis of low-cost and easily available CDs for environmental applications.

1. Introduction
Quantum dots are nanoparticles that have gained significant fame in diagnosis and labeling applications due to its intriguing optical (fluorescence) and electronic properties [1]. However, the synthesis process of quantum dots is not environmentally friendly as it involves the use of cadmium and arsenic heavy metals which makes them potentially hostile towards the biological applications [2,3]. In this scenario, carbon dots (CDs) synthesized from carbon precursors have emerged as an attractive alternative to quantum dots. CDs are oxygenous carbon nanoparticles with a size of less than 10 nm [4]. Owing to their low cytotoxicity and great water solubility, biocompatibility, and fluorescence properties, CDs have found promising application potential in various fields such as optical, optoelectronic, bioimaging, biomarking, solar cells, drug delivery, and photodynamic therapy [1,5–7].

The synthesis of CDs can be generally categorized into top-down (e.g. laser ablation, electrodeposition, arc discharge, etc.) and bottom-up (microwave, hydro and solvothermal, etc.) methods [8]. Top-down synthesis approaches break down larger carbon structures such as graphite and graphene into CDs, whereas bottom-up synthesis approaches generate CDs by decomposition, fusion or carbonization of small or large carbon precursors including both natural and synthetic polymers [8]. As compared to top-down synthesis approaches, the bottom-up processes are generally considered facile, cost effective,
and environmentally friendly without the need of harsh reagents or conditions [9–14]. Among these, the microwave synthesis method has gained increasing attention due to its fast reaction rates, milder reaction conditions, higher quantum yield, and lower energy usage [15].

Various studies have shown that CDs could be successfully produced from microwave synthesis method. For instance, Jusuf et al. [16] managed to obtain CDs from eggshell membrane ashes by using microwave irradiation technique within a short duration (60 s). The CDs was capable to degrade methylene blue (pollutant) under sunlight irradiation, indicating the photodegradation property of the sample [16]. In another study, Hinterberger et al. (2018) synthesized CDs with pH-dependent fluorescence color property from citric acid and o-phenylene-diamine as precursors via microwave-assisted hydrothermal approach [17]. The fluorescence emission color of the CDs solution could be tuned precisely and reproducibly from blue to white to yellow by controlling the pH. The aforementioned cases indicate that the precursors of CDs synthesis can come from a wide range of materials. However, the use of organic chemicals as precursors could potentially heighten the overall synthesis cost [9]. Hence, the use of natural materials and biomass waste (e.g. sugarcane bagasse pulp, carrot roots, tamarind, citrus peels, and used green tea) as precursors of CDs synthesis has received extensive interest recently, in line with the concept of green chemistry [18–22].

The use of non-toxic, easily available, and low-cost precursor for the synthesis of CDs could fulfill the green chemistry approach since the material is obtained from nature and thus the CDs produced are biocompatible in nature [23]. In this context, oil palm fronds (OPF) could be a promising carbon precursor for the synthesis of CDs. In Malaysia, more than 50 million ton of OPF biomass waste has been generated yearly from the palm oil industry, the most important agriculture sector in the country [24]. The use of OPF as carbon precursor for the synthesis of CDs for environmental application is feasible since it is available throughout the year and can be obtained at low to no cost. Furthermore, the conversion of OPF into CDs could help to valorize the biomass waste. Hence, this study aimed to utilize OPF as carbon precursor for the synthesis of CDs via microwave-assisted method. The impacts of the synthesis conditions (microwave irradiation power and period and synthesis solution) on the property and performance of CDs for heavy metal sensing were also investigated.

2. Methodology

2.1. Materials

The OPF (consist of leaflets and rachis) used as the precursor for CDs synthesis were collected from the oil palm in Universiti Kebangsaan Malaysia. Diethylene glycol (DEG) with 99.9 % purity was purchased from Sigma-Aldrich (USA) and ammonia solution 28 % was obtained from J.K. Baker (USA). Ultrapure water (UPW) with a quality of ~18.2 MΩ.cm at 25 ℃ produced from Sartorius Arium PRO (Fisher Scientific, USA) water purification system was used as solution in the synthesis and sample preparation. Lead (II) nitrate Pb(NO₃)₂ as the heavy metal was purchased from Merck, Malaysia.

2.2. Carbon Dots Synthesis

The collected OPF were dried under the sun for approximately 5 days to remove the moisture content of the sample. Afterwards, the OPF were cut into smaller pieces before ground and sieved to obtain the sample in fine powder form of 0.2 mm. The ground OPF samples were then mixed with 38 ml of DEG and 2 ml of ammonia solution to form a mixture with concentration of OPF powder of 10 g/L. The sample mixtures were sonicated for 30 min to homogenize the dispersion of OPF powder in the solution. The samples were subsequently heated in the microwave oven (Midea MM720CXM, Malaysia) at different heating power (low: 119 W, medium: 285 W, and high: 700 W) and duration ranging within 30-120 s. Table 1 summarized the synthesis condition for this experiment. After undergoing microwave irradiation process, the samples were cooled to room temperature before centrifuged at 10000 rpm for 20 min to remove bulk particles or agglomerates. The supernatant was collected and kept for further analysis and application testing.
Table 1. Synthesis conditions of carbon dots from OPF via microwave-assisted approach.

| Set | Microwave irradiation power (W) | Microwave irradiation time (s) |
|-----|-------------------------------|-----------------------------|
| A1  | 119                           | 30                          |
| A2  | 60                            | 60                          |
| A3  | 90                            | 90                          |
| A4  | 120                           | 120                         |
| B1  | 385                           | 30                          |
| B2  | 60                            | 60                          |
| B3  | 90                            | 90                          |
| B4  | 120                           | 120                         |
| C1  | 700                           | 30                          |
| C2  |                               | 60                          |
| C3  | 90                            | 90                          |
| C4  | 120                           | 120                         |

2.3. Characterization of CDs

Fourier Transformed Infrared (FTIR) (Nicolet, 6700, United States) was used to characterize the functional groups present on the OPF powder and synthesized CDs. The absorption spectra of the CDs were determined by Lambda 950 UV-visible spectrophotometer (Perkin Elmer, United States). Fluorescence spectrophotometer (FLS920, Edinburgh Instrument, United Kingdom) was used to determine the photoluminescence spectra and fluorescence intensity of the synthesized CDs. Transmission Electron Microscope (TEM) (Thermo Fisher, Talos 120 C, United States) was employed to obtain the high-resolution images of the CDs.

2.4. Detection of Lead (II) Nitrate

Testing solutions at different concentrations of lead (II) nitrate (20 ppm, 50 ppm, 100 ppm, and 150 ppm) were prepared for the evaluation of fluorescence quenching in the presence of heavy metal. Next, 5 ml of the as-synthesized CDs was mixed with the lead (II) nitrate solutions and the effectiveness of metal ions sensing was determined through the quenching of photoluminescence spectrum of CDs.

3. Results and Discussion

3.1. Characterization of CDs

Figure 1 illustrates the appearance of CDs synthesized under different conditions viewed under normal light and UV light (365 nm). As all the CDs solutions look the same under normal light (pale brownish), only one representative was included in figure 1. Since the CDs emitted green-blue fluorescence upon irradiated with UV light, it can be said that the OPF has been successfully converted to CDs. For benchmarking purpose, CDs synthesized with water and DEG medium (without ammonia solution) at microwave irradiation power of 385 W and time of 90 s were included too. It can be seen that CDs with medium irradiation power possessed the brightest green-blue fluorescence as compared to the rest. This could be attributed to the degree of carbonization where insufficient irradiation power (119 W) results in incomplete carbonization while excessive irradiation (700 W) causes over carbonization, where both scenarios lead to the formation of defect or degraded CDs. This observation aligned with the reported study where both incomplete carbonization and over carbonization (decomposition of precursor into...
ashes) would lead to the loss of the fluorescence property [25]. The effect of irradiation duration was uncertain and would be discussed based on other analysis. Meanwhile, the use of DEG as solution medium and ammonia solution as doping agent seemed to enhance the fluorescence of CDs as brighter light was observed for the sample set A, B, and C. Further discussion will be provided below by referring to other analysis results.

![Sample inside UV viewer chamber](image)

**Figure 1.** CDs viewed under normal light and UV (365 nm) viewer chamber.

To gain insight into the surface and structural information that contributed to the fluorescence property of CDs, FTIR, and TEM have been conducted. Considering that the FTIR results of all CDs sample were almost the same, only one spectra was displayed as in figure 2. The peak at 3386 cm$^{-1}$ could be assigned to O-H stretching while the presence of carbonyl functional group was revealed with C=O stretching at 1658 cm$^{-1}$. The peak at 1058 cm$^{-1}$ indicated the presence of C-O-C or C-O stretching. All these functional groups were normally known to contribute to the fluorescence property of CDs as reported in past literature [13,14,16,26]. Hence, the CDs synthesized from OPF possessed the typical functional groups responsible for its luminescent property.

![FTIR spectra](image)

**Figure 2.** FTIR spectra of CDs synthesized at microwave irradiation power of 119 W and duration of 120 s.
The size and shape of CDs were determined through TEM images as shown in figure 3. In general, all CDs were spherical in shape and with a size less than 10 nm, regardless of the synthesis conditions. This morphology was quite similar with the features reported in other studies [26,27]. The influence of irradiation power on the size of CDs was more apparent as compared to irradiation duration. As can be seen from figure 3, the sizes of CDs were between 3.0-5.0 nm, 2.0-3.5 nm, and 3.0-7.0 nm for microwave irradiation power of 117 W, 385 W, and 700 W, respectively. This could be an indication that the carbonization process was more appropriate for microwave irradiation power of 385 W, while under or over carbonization would lead to the formation of less perfect CDs. The size observation supported the fluorescence intensity as shown in figure 1.

![Figure 3. TEM images of CDs samples synthesized under different conditions (a) A3; (b) B4; (c) C1.](image)

### 3.2. Photoluminescence Property of CDs

Figure 4 (a) illustrates the photoluminescence spectra of CDs for each microwave irradiation power with the highest intensity and control sets of using ultrapure water and DEG as reacting medium (CDs synthesized with microwave irradiation power of 385 W and duration of 90 s). In general, the highest photoluminescence intensity was obtained within the shortest irradiation period of 30 s, regardless of microwave irradiation power (as can be seen in figure 4(b-d)). Nonetheless, prolonging the microwave irradiation duration was found to reduce the photoluminescence intensity for each set of CDs, with more drastic reduction recorded for high microwave irradiation power (700 W). This could be due to phenomena of over carbonization where under long period of exposure to high irradiation power destroyed the structure of CDs and thus resulted in the lower photoluminescence intensity [25]. Subsequently, the best CDs sample in set C (C1) recorded lower photoluminescence intensity as compared to set A and B (figure 4 (a)).

The CDs sample with the highest photoluminescence intensity was obtained at 385 W microwave irradiation power and duration of 30 s. The finding further strengthened the observation where set B CDs emitted the brightest luminescence light when viewed under UV light (figure 1). As mentioned previously, microwave irradiation at lower power could not lead to complete carbonization while higher irradiation power could damage to structure of CDs. Subsequently, the photoluminescence intensity was also affected and appeared to be weaker compared to microwave irradiation power of 385 W. Figure 4 also shows an interesting phenomenon where the photoluminescence intensity of CDs with DEG as the heating solution and ammonia as the doping solution was higher compared to sample with ultrapure water. This could be attributed to the higher boiling point of DEG, which allowed a more complete reaction for the formation of CDs through several possible mechanisms such as intermolecular dehydration and polymerisation that only happened at higher temperature [28]. In addition, the doping agent (ammonia solution) could enhance the photoluminescence property of the CDs.
3.3. Detection of Copper (II) Ions

The luminescent property of CDs is of great interest since the quenching of the absorbance could provide an indication of the presence of targeted compounds, e.g. pollutants [29]. This confers the CDs the potential to be used as a sensing material for environmental pollution detection purpose. In this study, the capability of CDs as heavy metal pollutant-copper (II) ions sensing has been evaluated by observing the changes of absorbance spectra with the addition of metal ions at different concentration. It can be seen from figure 5 that the UV-vis absorbance declined with the increase of copper (II) ions concentration, with a reduction range of 7-58 %. This indicated that the heavy metal ions could react with the oxygeneous functional groups present on the CDs surface through chelation for metal ion complexation [30,31]. The formation of complex between CDs and copper (II) ions would facilitate the electron/hole recombination annihilation, which subsequently lead to the reduction of absorbance [32,33]. The decline pattern of absorbance for other CDs (A1 and C1) followed the same trend as in figure 5 and hence was not included here. The range of absorbance decline of A1 CDs and C1 CDs was within 4-28 % and 13-43 %, respectively. The lower reduction of absorbance could be attributed to the under and over carbonization situation, where the amount of CDs was lesser or the property of CDs was damaged during the microwave irradiation process. Hence, it can be deduced that the CDs synthesized from low-cost and easily available OPF could be used as a quick pollutant detection material to cope with environmental pollution issues.

Figure 4. Photoluminescence spectra of CDs at excitation wavelength of 370 nm.
4. Conclusion
The OPF has been successfully converted into CDs via microwave-assisted synthesis approach with fluorescence property. It was discovered that microwave irradiation power has a more dominant effect on the fluorescence property as compared to microwave irradiation duration. Microwave irradiation at low (119 W) and high (700 W) power led to incomplete and over carbonization, respectively. This resulted in lower photoluminescence intensity as compared to CDs synthesized from microwave irradiation power of 385 W. On top of that, DEG as the reacting solution enabled a more complete formation of CDs and ammonia as the doping solution further enhanced the fluorescence property of the CDs. In terms of lead (II) ions detection, it was observed that the increase of lead (II) ion concentration reduced the UV-vis absorbance of the CDs solution, indicating there was interaction between CDs and lead (II) ions. Overall, the decline of absorbance values indicated the potential of the CDs synthesized from OPF to be used for lead (II) sensor and detection.

Reference
[1] Baker S N and Baker G A 2010 Luminescent carbon nanodots: Emergent nanolights Angew. Chemie - Int. Ed. 49 6726–44
[2] Tan W B, Huang N and Zhang Y 2007 Ultrafine biocompatible chitosan nanoparticles encapsulating multi-coloured quantum dots for bioapplications J. Colloid Interface Sci. 310 464–70
[3] Cho S J, Maysinger D, Jain M, Röder B, Hackbarth S and Winnik F M 2007 Long-term exposure to CdTe quantum dots causes functional impairments in live cells Langmuir 23 1974–80
[4] Jia X, Li J and Wang E 2012 One-pot green synthesis of optically pH-sensitive carbon dots with upconversion luminescence Nanoscale 4 5572–5
[5] Hu L, Sun Y, Li S, Wang X, Hu K, Wang L, Liang X J and Wu Y 2014 Multifunctional carbon dots with high quantum yield for imaging and gene delivery Carbon N. Y. 67 508–13
[6] Shen J, Zhu Y, Yang X and Li C 2012 Graphene quantum dots: Emergent nanolights for bioimaging, sensors, catalysis and photovoltaic devices Chem. Commun. 48 3686–99
[7] Liu H, Ye T and Mao C 2007 Fluorescent carbon nanoparticles derived from candle soot Angew.
Chemie - Int. Ed. 46 6473–5

[8] Chu K W, Lee S L, Chang C J and Liu L 2019 Recent progress of carbon dot precursors and photocatalysis applications Polymers (Basel). 11 689

[9] Liang Q, Ma W, Shi Y, Li Z and Yang X 2013 Easy synthesis of highly fluorescent carbon quantum dots from gelatin and their luminescent properties and applications Carbon N. Y. 60 421–8

[10] Bhunia S K, Saha A, Maity A R, Ray S C and Jana N R 2013 Carbon nanoparticle-based fluorescent bioimaging probes Sci. Rep. 3 1473

[11] Zhang Z, Sun W and Wu P 2015 Highly photoluminescent carbon dots derived from egg white: Facile and green synthesis, photoluminescence properties, and multiple applications ACS Sustain. Chem. Eng. 3 1412–8

[12] Kumawat M K, Srivastava R, Thakur M and Gurung R B 2017 Graphene quantum dots from mangifera indica: Application in near-infrared bioimaging and intracellular nanothermometry ACS Sustain. Chem. Eng. 5 1382–91

[13] Liao J, Cheng Z and Zhou L 2016 Nitrogen-doping enhanced fluorescent carbon dots: Green synthesis and their applications for bioimaging and label-free detection of Au3+ ions ACS Sustain. Chem. Eng. 4 3053–61

[14] Sahu S, Behera B, Maiti T K and Mohapatra S 2012 Simple one-step synthesis of highly luminescent carbon dots from orange juice: Application as excellent bio-imaging agents Chem. Commun. 48 8835–7

[15] Xu M, He G, Li Z, He F, Gao F, Su Y, Zhang L, Yang Z and Zhang Y 2014 A green heterogeneous synthesis of N-doped carbon dots and their photoluminescence applications in solid and aqueous states Nanoscale 6 10307–15

[16] Jusuf B N, Sambudi N S, Ismaeni I and Samsuri S 2018 Microwave-assisted synthesis of carbon dots from eggshell membrane ashes by using sodium hydroxide and their usage for degradation of methylene blue J. Environ. Chem. Eng. 6 7426–33

[17] Vanessa H, Wenshuo W, Cornelia D, Simon W, Martin T and Wolfgang P 2018 Microwave-assisted one-step synthesis of white light-emitting carbon dot suspensions Opt. Mater. (Amst). 80 110–9

[18] D’souza S L, Chettiar S S, Koduru J R and Kailasa S K 2018 Synthesis of fluorescent carbon dots using Daucus carota subsp. sativus roots for mitomycin drug delivery Optik (Stuttg). 158 893–900

[19] S. T and D. R S 2016 Green synthesis of highly fluorescent carbon quantum dots from sugarcane bagasse pulp Appl. Surf. Sci. 390 435–43

[20] Hsu P C, Chen P C, Ou C M, Chang H Y and Chang H T 2013 Extremely high inhibition activity of photoluminescent carbon nanodots toward cancer cells J. Mater. Chem. B 1 1774–81

[21] Asha Jhonsi M and Thulasi S 2016 A novel fluorescent carbon dots derived from tamarind Chem. Phys. Lett. 661 178–94

[22] Chatzimitakos T, Kasouni A, Sygellou L, Avgneropoulos A, Troganis A and Stalikas C 2017 Two of a kind but different: Luminescent carbon quantum dots from Citrus peels for iron and tartrazine sensing and cell imaging Talanta 175 305–12

[23] Himaja A L, Karthik P S, Sreedhar B and Singh S P 2014 Synthesis of carbon dots from kitchen waste: Conversion of waste to value added product J. Fluoresc. 24 1677–73

[24] Ooi Z X, Teoh Y P, Kunasundari B and Shui S H 2017 Oil palm frond as a sustainable and promising biomass source in Malaysia: A review Environ. Prog. Sustain. Energy 36 1864–74

[25] Tan X W, Romainor A N B, Chin S F and Ng S M 2014 Carbon dots production via pyrolysis of sago waste as potential probe for metal ions sensing J. Anal. Appl. Pyrolysis 105 157–65

[26] Mewada A, Pandey S, Shinde S, Mishra N, Oza G, Thakur M, Sharon M and Sharon M 2013 Green synthesis of biocompatible carbon dots using aqueous extract of Trapa bispinosa peel Mater. Sci. Eng. C 33 2914–7

[27] Yang Y, Cui J, Zheng M, Hu C, Tan S, Xiao Y, Yang Q and Liu Y 2012 One-step synthesis of
amino-functionalized fluorescent carbon nanoparticles by hydrothermal carbonization of chitosan Chem. Commun. 48 380–2

[28] He G, Shu M, Yang Z, Ma Y, Huang D, Xu S, Wang Y, Hu N, Zhang Y and Xu L 2017 Microwave formation and photoluminescence mechanisms of multi-states nitrogen doped carbon dots Appl. Surf. Sci. 422 257–65

[29] Ang W L, Boon Mee C A L, Sambudi N S, Mohammad A W, Leo C P, Mahmoudi E, Ba-Abbad M and Benamor A 2020 Microwave-assisted conversion of palm kernel shell biomass waste to photoluminescent carbon dots Sci. Rep. 10 1–15

[30] Praneerad J, Thongsai N, Supchocksoonthorn P, Kladsomboon S and Paoprasert P 2019 Multipurpose sensing applications of biocompatible radish-derived carbon dots as Cu 2+ and acetic acid vapor sensors Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 211 59–70

[31] Su Q, Wei X, Mao J and Yang X 2019 Carbon nanopowder directed synthesis of carbon dots for sensing multiple targets Colloids Surfaces A Physicochem. Eng. Asp. 562 86–92

[32] Sun S, Guan Q, Liu Y, Wei B, Yang Y and Yu Z 2019 Highly luminescence manganese doped carbon dots Chinese Chem. Lett. 30 1051–4

[33] Tabaraki R and Sadeghinejad N 2018 Microwave assisted synthesis of doped carbon dots and their application as green and simple turn off–on fluorescent sensor for mercury (II) and iodide in environmental samples Ecotoxicol. Environ. Saf. 153 101–6

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