Blue luminescence carbon quantum dots derived from oil palm empty fruit bunch biomass

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Abstract. Carbon quantum dots (CQDs) have attracted tremendous attention for their interesting properties such as excellent chemical and photo stability, good water dispersibility, biocompatibility and possessing outstanding photoluminescence (PL) properties. In this study, oil palm biomass is used as the carbon precursor to produce CQDs and exhibit high luminescent properties. However, a large amount of biomass produced by the oil palm industry is either burnt in the open air or disposed in waste ponds and contributes to global climate change via emissions of carbon dioxide and methane. Hence, synthesis the CQDs from oil palm biomass by hydrothermal treatment method has formed excellent properties in optical properties that could be comparable to semiconductor quantum dots. The results have shown the diameter size of CQDs in the range of 2-5 nm. While, the optical properties, UV-vis spectrum of CQDs have given a strong absorption at 282 nm and obtains in brown color under visible light and emitting blue luminescence under 365 nm of UV lamp. Furthermore, PL spectra of CQDs have shown excitation and emission wavelength at 360 nm and 450 nm, respectively. This is attribute to the excitation-wavelength dependent of PL properties. Hence, the spectra from FTIR showed the existence of hydroxyl and carboxyl groups on the CQDs would have originated from lignocellulosic materials, thus resulted in excellent water stability and solubility properties of CQDs. The presented study is the green approach reprocessed biomass from waste to materials with excellent optical properties that could utilize in various field of applications.

1. Introduction

Carbon quantum dots (CQDs) have recently emerged as a new family of 0D nano-carbon materials. They are spherical nanoparticles with sizes below 10 nm and showed excitation-wavelength-dependent of photoluminescence (PL) behavior. They are usually known to develop the intrinsic optical properties and also caused existing the surface energy trap states and surface passivation [1]. However, both the optical absorption and fluorescence emissions in CQDs do not originate from a band gap but instead are due to π-domain and radiative recombination of the surface-confined electrons and holes that are difference from conventional semiconductor QDs [2]. Compared with traditional organic dyes and semiconductor quantum dots, CQDs show distinguished properties such as stable photoluminescence, easy surface functionalization, good biocompatibility, and low toxicity [3].

The oil palm industry is one of the larger contributors to the lignocellulosic-rich, solid waste materials, and generated in the field. The mill residues include mesocarp fiber, shell, palm kernel cake, boiler ash, palm oil mill effluent, bunch ash, and empty fruit bunches are contained percentage of
lignocellulose. From each bunch of the fresh palm fruit, approximately 21% of palm oil, 6–7% of palm kernels, 14–15% of palm fibers, 6–7% of palm shells, and 23% of empty fruit bunches can be obtained [4]. It is alarming that wastes generated from oil palm activities are posing major disposal problems which are generally left for biodegradation and ultimately end up to air or dust pollution [4]. Therefore, there is a need for technology, cost-effective, energy balance and environmental consideration in balanced properties in order to resolve the utilization of oil palm wastes. In an attempt to manage oil palm wastes in a more convenient way, we used oil palm as a carbon source for the synthesis of CQDs.

Recently, green production methods using environmentally friendly green carbon precursors have been investigated in attempts to achieve a simple, cost-effective, environmentally friendly method with exciting properties. There are various groups synthesize carbon dots from green carbon precursors that are reported by Wang et al. 2016, using papaya as a carbon source for carbon dots for effective fluorescent sensing of iron (III) and E. coli [5]. Tyagi et al. also reported by using green synthesis from lemon peel waste can enhance the excellent photoluminescent (PL) and exhibit higher quantum yield for application in sensing and photocatalysis [6]. Furthermore, Zhou et al. have been reported that synthesis watermelon peels as carbon source haven been successfully applied in live-cell imaging, and can serve high-performance in optical imaging probes [7]. Hence, in this study we focus the use of green material from oil palm empty fruit bunch biomass to produce CQDs due to their advantages in reducing chemical exposure, reducing waste, producing cheap, renewable and abundant biomass, and having potential to scale-up their applications in various fields.

In recent years, many methods were developed for the synthesis of CQDs, including electrochemical, ultrasonic, laser ablation, chemical oxidation, microwave methods and hydrothermal treatment [8]. Among them, hydrothermal treatment synthesis was considered to be a simple, cost-effective and efficient way to prepare CQDs compared with traditional semiconductor quantum dots and organic dyes that used complicated raw materials with large amounts of strong acid and tedious processes that create problems to the environment. For example, Sahu at al. reported by synthesis CQDs using hydrothermal carbonization using low-cost wastes as a precursor, Liu et al. adopted hydrothermal treatment of Grass to produce CQDs and Zhao et al. also reported their synthesis method by hydrothermal for CQDs to study its photoluminescence [9-11].

Herein, the blue luminescence CQDs were prepared by hydrothermal treatment in which oil palm empty fruit bunch biomass was used as carbon precursor material and provide the capability for large-scale synthesis and easy to scale-up. The obtained CQDs give high luminescence optical properties and make this fluorescence nanoparticle be applied in the large scale of applications.

2. Experimental section
2.1. Synthesis of CQDs
CQDs was synthesized from oil palm empty fruit bunch biomass by hydrothermal method. 6 g of oil palm powder was added to 150 mL of deionizing water. Then the mixture was transferred into a 200 mL Teflon lined autoclave and tightly sealed to maintain the inbuilt pressure. The autoclave was heated at 200 °C for 3 hours. The reaction vessel was allowed to cool in room temperature and the solution was centrifuge at 1000 rpm for 30 minutes. The solution was filtered through a 0.2 μm filter to remove micron-sized particles. The final solution was stored at 4 °C for further characterization [12].

2.2. Characterization
The morphology and the microstructure of the CQDs were analyzed by a transmission electron microscope model TALOS L 120C using an accelerating voltage of 120 kV. The TEM samples were prepared by drop-casting CQDs solution on to a carbon-coated copper grid and dried under room temperature before the analysis. Dynamic light scattering (DLS) measurements were performed on SZ-100, Horiba Scientific instrument at a constant scattering angle of 90°. For the absorption spectra and photometric studies were carried out on a Shimadzu UV-1700 UV-Vis spectrophotometer [13].
The steady-state photoluminescence (PL) spectra were taken using fluorescence spectrometer on a Perkin Elmer spectrophotometer equipped with a lamp in range (320-400 nm) as excitation wavelength sources. Fourier Transform Infrared Spectroscopy (FTIR) spectroscopy is used to analyze the synthesis CQDs for their functional groups. FTIR spectrum (Model GX) with transmission mode ion range 400-4000 cm\(^{-1}\) with accumulation of 32 scans and 2.0 cm resolution whereas the elemental and compositional analysis of CQDs was measured by XPS using a Kratos/Axis Ultra DLD is used [14].

3. Result and discussion

Morphological and size characterization of synthesis CQDs from oil palm biomass was analyzed with transmission emission spectroscopy (TEM). Figure 1(a) shows the TEM image clearly reveal that CQDs are spherical in shape with a narrow size distribution ranging between 2 to 5 nm in diameter as indicated in histogram inset of Figure 1(a). The result was further verified by dynamic light scattering (DLS) analysis as shown in Figure 1 (b), indicated the average particle size of CQDs was measure to about 7 ± 1 nm.

![Figure 1](image)

**Figure 1.** (a) TEM image and size distribution of CQDs synthesized from oil palm biomass (b) DLS Size distribution by the intensity of the CQDs

FTIR analysis was performed to analyse the presence of polar functional groups on the surface of CQDs. Figure 2 (a) shows a broad absorption band at 3309 cm\(^{-1}\) corresponding to the stretching vibrational characteristic of (O–H). The peak at 1595 cm\(^{-1}\) clearly indicated that surface CQDs containing carboxylic groups (\(-\text{COO}\)–). Absorption bands at 896, 1025, 1245 and 1595 cm\(^{-1}\) are assigned to the (C–C), (C–O), (C=C) and (C=O) respectively. FTIR spectrum revealed the presence of hydrophilic surface functional groups over the CQDs surface, thus imparts the excellent water solubility and stability [6]. X-ray photoelectron spectroscopy (XPS) was used for further confirmation of the different functional groups on the surface of CQDs. The XPS spectrum for CQDs shown in Figure 2(b) reveal three types of carbon bonds indicated C=C, C–O, and C=O at 284.5, 286.1 and 288.2 eV, respectively which correspond to sp\(^3\) and sp\(^2\) carbons. The presence of \(-\text{OH/\text{C-O-C}}\) and \(-\text{C=O}\) reveal the hydrophilic surface functionalization of CQDs which is consistent with FTIR and zeta potential analysis [15].
Elemental analysis revealed that the composition of oil palm to be C (71.23 wt%), N (1.7 wt%) and O (23.5 wt%). The high carbon and oxygen content suggest that the obtained particles are probably nano-scaled carbonaceous material with a large number of carboxyl groups on the surface [12]. Compared to other biomass like coconut shell, the composition has been estimated to be 29.35% lignin, 24.20% cellulose, 38.56% hemicellulose with the element of C (49.6 wt%), H (7.3 wt%), N (0.22 wt%) and O (42.7 wt%) [16]. Chemical content of rice husk consists of 50% cellulose, 25-30% lignin, and 15-20% silica. As rice husk contains a high concentration of silica (15-28 wt%) the most common approaches to take advantage of rice husk are to prepare silicon-based materials instead of preparing the carbon-based materials [17,18]. The biochemical composition of rice straw and wheat straw is characterized by a typical composition of an agricultural-based lignocellulosic residue and it contains on average 30 – 45% cellulose, 20 – 25% hemicellulose, 15 – 20 % lignin, as well as a number of minor organic compounds [19]. Thus, it shows that the degree of surface functionalization is depended on the type of biomass precursor, which in turn reflects variations in optical behavior. Therefore, the differences in biomass are used as precursors for synthesis CQDs will give several properties of CQDs.

![Figure 2](image1.png)

**Figure 2.** (a) FTIR spectrum of CQDs (b) High-resolution scans of XPS for the C1s region of CQDs from oil palm biomass.

![Figure 3](image2.png)

**Figure 3.** (a) UV-vis absorption spectrum of CQDs from oil palm biomass and inset with photograph images of solution CQDs under white light (brown color) and UV lamp 365 nm (blue color) (b) PL excitation and emission spectra of CQDs in aqueous solutions.
The UV-vis absorption spectrum of CQDs is illustrated in Figure 3(a) have good aqueous solubility and shows brown color under white light and blue color under 365 nm UV lamp. The UV-vis spectrum shows a strong absorption at 282 nm thus indicated CQDs have emitted blue emission. This is attributed to the n-π* transition of the C=O band and π-π* transition of the conjugated C=C band [20,21]. However, CQDs aqueous dispersion shows zeta potential value of (-15.67 mV) confirming the presence of high density negatively charge of carboxylic groups on the CQDs surface. Figure 3(b) shows the photoluminescence spectra of CQDs exhibited the excitation and emission wavelength at 350 nm and 450 nm. The emission wavelength is in the range of 400-500 nm and emerged as a blue peak at 450 nm. They are two main reasons for initiating of these PL spectra behavior on CQDs, which is the distribution of the different surface energy traps on the CQDs and the different sizes of CQDs distribution [22]. From the result, clearly shown that PL intensity is dependent on the concentration dilution of the CQDs. The PL intensity is increased, by increasing the concentration dilution of the CQDs and this may cause by the decreasing interactions among the different polar groups at low concentration [23]. However, at too high concentrations of CQDs, the forming of agglomeration is due to the presence of the high amount of polar functionality. Besides that, PL intensity is also depending on the number of CQDs particles excited at a particular wavelength. The strong emission peak of PL located at 450 nm has been observed with an excitation wavelength of 360 nm. This happened due to the CQDs with the smaller size (5 to 17 nm) will get excited at a lower wavelength, while those with the larger size (5 to 35 nm) will get excited at a higher wavelength [24]. Furthermore, another reason for the excitation dependent of PL behavior for CQDs is the nature of their surface [25]. Where the optical behaviour of CQDs is due to the surface energy traps and quantum confinement effects can cause the tuneable of emissions from particles states thus effect on their sizes.

4. Conclusions
In conclusion, carbon quantum dots with high luminescence properties were synthesized using facile, cost-effective and environmentally friendly process by utilizing of oil palm biomass inconvenient way. The hydrothermal synthesis possesses the merit of green synthesis and resource-saving process with a short reaction time. The CQDs exhibit excellent optical properties by emitting blue fluorescence, the existence of hydroxyl and carboxyl groups which originated from OPEFB lignocellulose materials shows the excellent water stability and solubility properties of CQDs, thereby facilitating their wide range of applications in biomedical, energy storage, water purification along with many more future applications.

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