SYNTHESIS OF CARBON DOTS FROM EMPTY FRUIT BUNCH BIOCHAR VIA AN ACID-FREE HYDROTHERMAL METHOD

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Abstract: Carbon dots have gained much interest due to their outstanding optical and electrical properties, making them useful for a wide range of applications. Here Empty fruit bunch (EFB) biochar was used as a carbon source in a straightforward, environmentally friendly, and reproducible hydrothermal method for producing carbon quantum dots. In this study, the role of the hydrothermal process was seen and studied by comparing the shape and fluorescence. Exciting results from HRTEM show that the carbon quantum dots in the sample are 4 nm in size. The obtained CD emits bright blue luminescence, and the absorption peak of the carbon dots was observed in the UV region with maximum absorption at 205 nm and 322 nm. The light CD shows an intense sky blue color upon illumination by a UV-light source at 365 nm. The intensity of the photoluminescence (PL) spectra sharply increases with decreasing concentration of carbon dots. Meanwhile, the CD exhibited excitation-dependence, photo-stability, and well dispersibility. These results suggest that the present CD are potential applications in optoelectronics and imaging.
Keywords: Carbon Dots; Empty Fruit Bunch; Hydrothermal Methods; Waste

Abstrak: Karbon dots telah menarik banyak perhatian karena sifat listrik dan optik yang luar biasa, sehingga dapat digunakan untuk berbagai aplikasi. Penelitian ini, menggunakan biochar tandan buah kosong (EFB) sebagai sumber karbon dengan metode hidrotermal yang ramah lingkungan untuk menghasilkan karbon dots. Hasil HR-TEM yang menarik menunjukkan bahwa sampel karbon dots berukuran 4 nm. Karbon dots yang diperoleh memancarkan sinar biru terang dan puncak serapan titik karbon diamati pada spektrofotometri Uv-Vis dengan serapan maksimum pada 205 nm dan 322 nm. Intensitas karbon dots menunjukkan warna biru langit di cahaya UV pada 365 nm. Intensitas spektroskopi luminesens meningkat tajam dengan menurunnya konsentrasi titik karbon. Sementara itu, karbon dots menunjukkan eksitasi, stabilitas, dan dispersibilitas baik. Hasil ini menunjukkan bahwa karbon dots dapat digunakan pada beberapa aplikasi seperti dalam optoelektronik dan pencitraan.
Kata kunci: Karbon dots; Tandan Buah Kosong; Metode Hidrotermal; Limbah.

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Introduction

Carbon dots (CD) are a novel class of carbon nanoparticles during the extraction of single-walled carbon nanotubes. These nanoparticles possess a size range of less than 10 nm (González-González et al., 2022). CD, a new family of nanomaterials, finds wide attention among the scientific community due to their unique properties, including high chemical stability, good biocompatibility, low toxicity, catalytic properties, electrical properties, electrical conductivity, and excellent optical properties, and minimal photobleaching. The CD has several applications, especially photoluminescence, sensors, energy sources, and bioimaging agents (Marpongahtun et al., 2018). The most common methods for synthesizing CD are chemical oxidation, ultrasonic synthesis, hydrothermal carbonization, solvothermal synthesis, microwave synthesis, and laser ablation. Of these, hydrothermal carbonization is one of the most facile methods. Recently, it has proved to be an eco-friendly, simple, affordable, and soft chemical route for synthesizing CD in aqueous media, producing excellent fluorescent probes for bioimaging applications (Wang & Hu, 2014).

Synthesizing can be divided into top-down and bottom-up approaches. Top-down approaches involve methods that can derive carbon dots from large carbon molecules, such as activated carbon and graphite carbon nanorods. On the other hand, bottom-up approaches extract carbon dots from carbon-containing precursors, such as citric acid, table sugar, glucose, fruits, and vegetables. Top-down approaches like ultrasonic-assisted synthesis, laser-assisted synthesis, and chemical oxidation are usually not preferred due to disadvantages, such as high processing cost, complex procedures, and energy-intensive (J. Liu, Li, & Yang, 2020). Bottom-up approaches, especially the hydrothermal method, are recommended in synthesizing CD, showing its low cost, controlled morphology, and facile synthesis method (Choi, Choi, Kwon, & Kim, 2018). During the CD synthesis process, variation in hydrothermal temperature affects the particle sizes of CD. This condition is because the hydrothermal process consists of carbonization and dehydration of the carbon core. Apart from that, functionalization on CD surfaces has a high impact as it assists in enhancing the performance of the carbon nanoparticles. Functionalization provides more surface functional groups on CD structure, allowing the CD to be utilized in broad applications (Han, He, Pan, Liu, & Hu, 2020).

This study is the first to synthesize carbon dots from biochar using aquadest as a non-chemical solvent and an acid-free hydrothermal process without chemical reagents. Palm oil industry waste is generated during the palm oil processing process. This type of waste is classified into solid waste, liquid waste, and gas waste. EFB contains cellulose of 45.95%, hemicellulose of 16.49%, and lignin of 22.84% (Ahmad, Rahmad, Rita, & Noorjannah, 2022). However, the most dominant content in EFB is cellulose. EFB is one of the by-products in the

form of solids from the palm oil processing industry (Gea et al., 2018). EFB have considerable potential to be exploited. So far, EFB has only been used as fertilizer, alternative material for filling car seat cavities, making mattresses or mattresses, and as a raw material for making paper. The large amount of cellulose contained in EFB can be used to manufacture small fluorescence nanomaterials commonly referred to as CD (Rani et al., 2021).

Materials and Methods

Materials

EFB from North Sumatra is the main raw material used to make carbon dots. deionized water is a non-chemical solvent purchased from CV. Rudang Jaya

Synthesis of Carbon Dots

EFB was cleaned with deionized water. The pulp was dehydrated in sunlight for 72 h before igniting at 70°C in the air atmosphere to form a carbon matrix. Briefly, 2 g of EFB was mixed with 25 mL of double-distilled water. The isolated precursor was shifted entirely to the autoclave at a stable temperature of 200°C for 6 h. The reactive mixture solution was ultrasonicated for 1 h and centrifuged for 60 min at 5000 rpm to remove fine undissolved particles. Eventually, the solid black precipitate was removed, and the supernatant liquid was stored for further characterization and use.

Characterization

HRTEM images were collected using a JEOL/JEM2100 microscope (operated at 200 kV). The FTIR spectrum was recorded with an FTIR spectrometer (PerkinElmer spectrometer) in the spectral range of 4000−400 cm^{-1} at ambient temperature. CD's linear optical absorption spectrum was recorded using a Shimadzu spectrophotometer (UV-1800), and the sample was immersed in water. Fluorescence studies were carried out with a single-beam PerkinElmer fluorescence spectrometer (model LS45) at ambient temperature (RT).

Result and Discussion

Optical Properties of CD

Using UV-Vis absorption and Photoluminescence (PL) spectroscopy, the optical properties of CD were studied and compared to those of EFB. As seen in Figure 1, the CD optical absorption peak was in the UV region, with a peak at 205 nm and a maximum at 322 nm. It was caused by the π-π* transition of the conjugated C=C bond and the n-π* transition of the C=O band (De & Karak, 2013). It can be seen that the CD in solution has a different color in daylight (greyish) and glows blue-green when exposed to UV light.

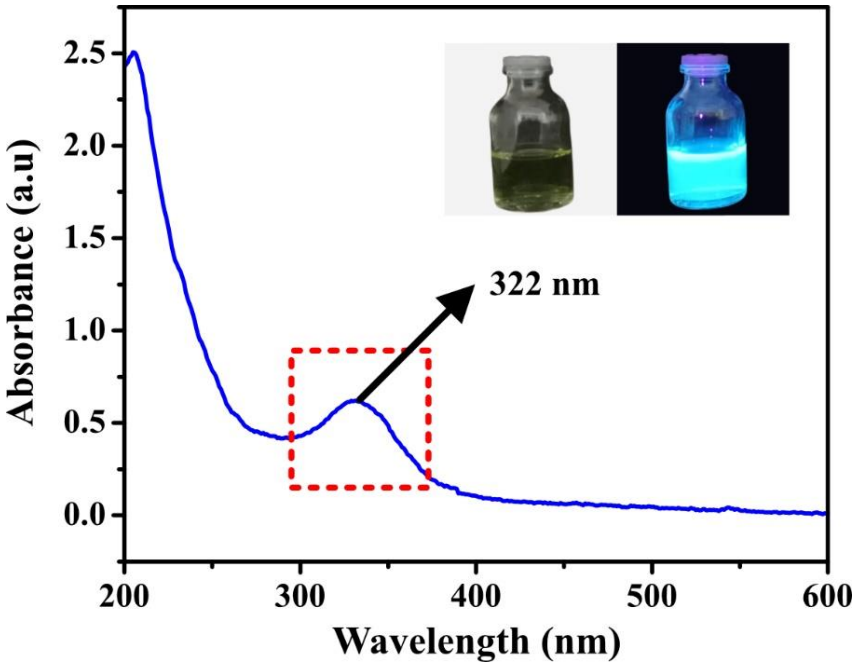

Figure 1. Optical spectra of the supernatant obtained from CD

A detailed PL study was done to find out about CD optical properties. The classic characteristic of CD is that the photoluminescent behavior depends on the emission wavelength and the emitter size. However, because the exact mechanism of how CD affects PL is hard to understand, this is still up for discussion. The plausible reasons for the size-dependent PL behavior are the different particle sizes of CD and the distribution of the different surface energy traps in CD (Jamaludin, Tan, Zaman, Sadrolhosseini, & Rashid, 2020). The size of the CD probably explains why the location of the emission peak is different. Like traditional semiconductor quantum dots, as the size of the CD gets smaller, the energy gap gets more significant, and vice versa. The larger particle will be excited at relatively longer wavelengths, while the smaller particle will be excited at relatively shorter wavelengths. So, the intensity of the PL depends heavily on how many particles are excited at a specific wavelength (De & Karak, 2013).

As a function of the wavelengths used to excite, the PL spectra of CD are shown in Figure 2. PL spectra of CD show an excitation wavelength of 460 nm. It is likely because most particles are excited at this wavelength. As the excitation wavelength gets longer, the emission peak moves to a longer wavelength. It shows that the intensity of both emission and PL depends on the wavelength of the excitation. PL spectra of CD behavior are also affected by how excited they are because of how their surfaces are made. Functional groups like hydroxyl, carbonyl, and carboxyl could cause a series of emitting traps between the π and π^* of C-C if they are on CD. So, it is thought that both the side effects and the surface defects affect the PL mechanism (De & Karak, 2013).

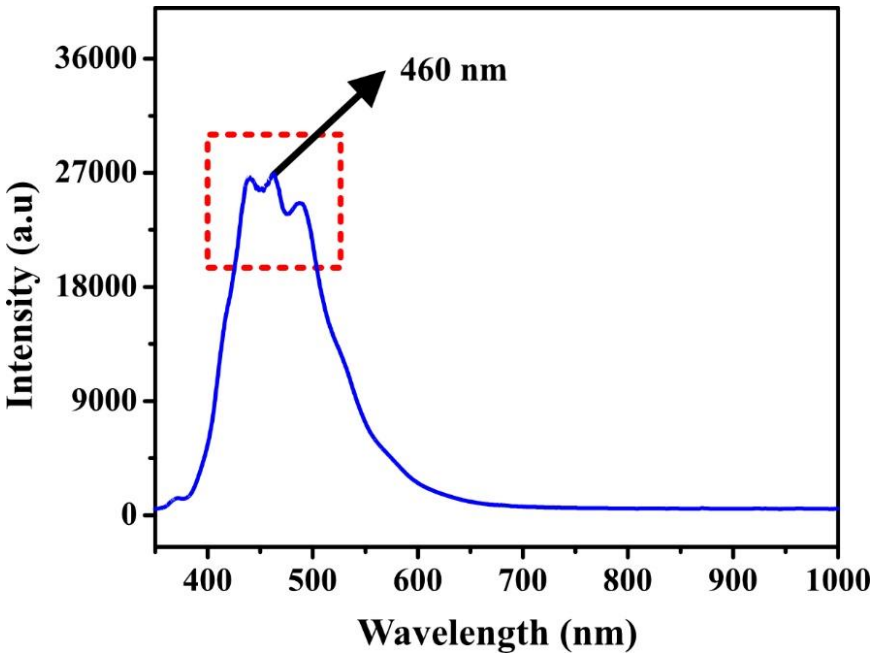

Figure 2. The PL spectrum of CD

By comparing the integrated PL intensities and the absorbance peak values of the CD, the quantum yield (QY) was calculated. Also, PL spectra were measured using an excitation wavelength of 300 nm. To improve the accuracy of measurements, the variation of the integrated intensity of fluorescence spectrum with absorbance at the excitation wavelength of the test sample and the standard sample was used to calculate the quantum yield using Equation (Yi et al., 2021):

$$QY=QY_{ref}\times\frac{\eta^2}{\eta^2_{ref}}\times\frac{I}{A}\times\frac{A_{ref}}{I_{ref}}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where QY_{ref} represents QY From quinine sulfate (0.54), η represents refractive solvent, η_{ref} Represent as refractive of quinine sulfate, I represent fluorescence intensity emission, I_{ref} represents intensity emission ref, A represents wavelength, and A_{ref} represents the reference wavelength.

The intensity of the PL spectra sharply increases with decreasing concentration of carbon dots. It may be due to decreasing interactions among polar groups at low concentrations. Using quinine sulfate as a reference quantum yield of carbon dots in an aqueous solution was measured at an excitation wavelength of 350 nm and was found to be 0.48 (Y. Liu et al., 2022). This value is lower than the literature-reported values for non-passivating CD. Thus the PL characteristic of the prepared carbon dots is promising for their different possible applications. In biological detection, carbon dots can be applied at low

concentrations as the PL intensity is sensitive to the concentration of carbon dots, whereas, at low concentrations, the variation of PL intensity is negligible.

Analysis of FTIR

The FTIR spectrum of carbon dots in Figure 3 shows the functional groups associated with the CD surface. The presence of these functional groups imparts excellent solubility in water without further chemical modification. The presence of such functional groups shows an absorption peak of 3265 cm^{-1}, which is the hydroxyl region of O-H, in the area of 2325 cm^{-1} indicating the C-H group. The wavelength at 2124 cm^{-1} shows the absorption area of C=C. A sharp peak area is obtained at a wavelength of 1640 cm^{-1}, which is a typical absorption of the CO functional group (Chang et al., 2022).

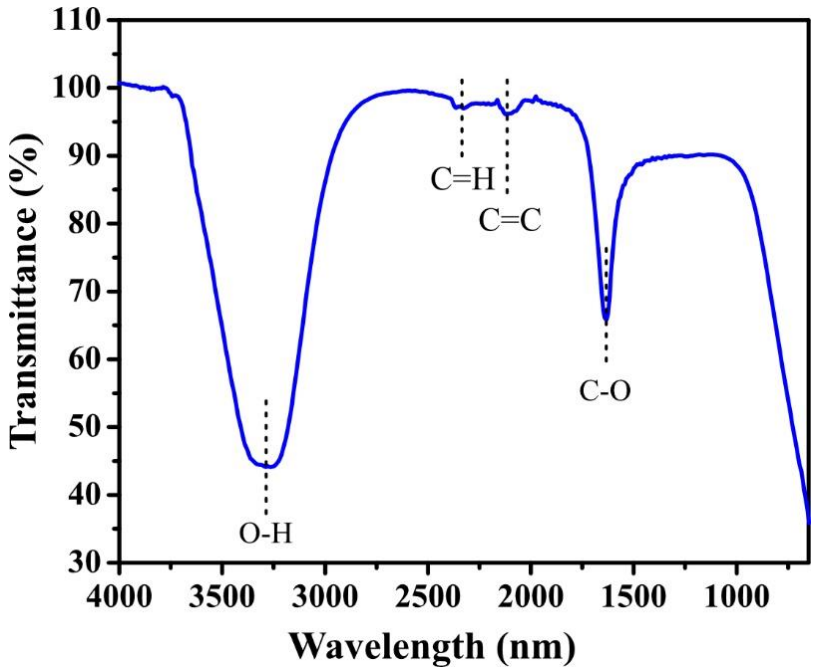

Figure 3. FTIR spectrum of CD

HRTEM Analysis

HRTEM images of CD are shown in Figure 4 with a particle size of 4 nm. The success rate of the green synthesis hydrothermal approach in producing CD was confirmed. The lattice fringes of CDs with an interplanar distance d of ~0.228 nm (inset fig.4). It was found from the CDs distribution curve that particles are distributed randomly (Pandiyan et al., 2020). From this research, it can be concluded that heating temperature affects fluorescence. If the temperature is higher than the efficiency of quantum, the fluorescence properties decrease. So,

the higher the temperature affects, the more excellent outside conversion results in reduced quantum efficiency (Marpongahtun et al., 2018).

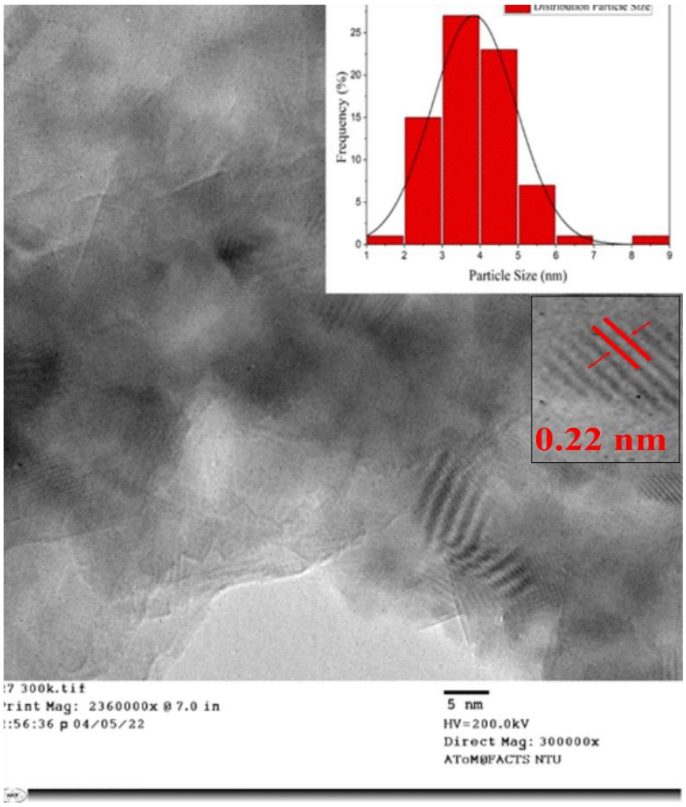

Figure 4. High-resolution transmission electron microscopy (HRTEM) of CD

Possibility mechanism for the extraction of CD

This study determined the hydrothermal process for easily extracting CD from EFB biochar in one step. This method used solid biochar made from agricultural waste as the carbon source and a very common solvent as the liquid medium. Interestingly, this method is neither strong acids nor a surface passivation step after the chemical reaction is needed. The hydrothermal reaction is based on the fact that substances dissolve easily in solvents at high pressure and temperature and that the dissolved material can be later extracted from the liquid phase. The relatively high temperature of the distilled water mixture compared to their respective boiling points is an essential part of the process. As the temperature increases, the vapor pressure increases, and the water's diffusion rate and reactivity change from what they were at room temperature. During the hydrothermal process that allowed CD to be extracted, oxygen-rich functional groups may have formed on the surface and edges of CD.

An illustration of the one-step CD hydrothermal-extraction process is shown in Figure 5. The extracted CD causes fluorescence under UV light and has high photoluminescence under different wavelengths of radiation. The blue fluorescent

CD also shows a broad PL peak that moves as the excitation wavelength increases. It might be due to the quantum confinement effect and edge defects. The unique behavior of excitation-dependent photoluminescence showed that the reaction products must be photoluminescence (He et al., 2018; Xu et al., 2019). EFB biochar, made without using the hydrothermal process, did not fluoresce, meaning that CD could not be extracted from it. EFB and CD have similar chemical compositions and surface states, which suggests that the hydrothermal process can pull the quantum dots out of the EFB biochar and into the dispersive medium. As we talked about earlier in the morphological study, it was shown that the EFB biochar already has dots that are almost the same size and structure. These quantum dots are almost spherical and are all the same size, ranging from 1 to 6 nm. The results suggest that CD was extracted during the hydrothermal process. Based on the results of these characterizations, the CD was successfully extracted with good water solubility and strong fluorescence properties in this work.

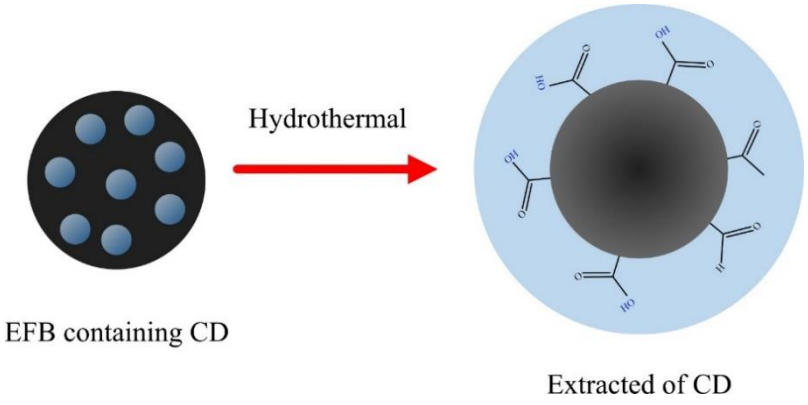

Figure 5. Illustration possibility mechanism for the extraction of CD

Conclusion

The resulting hydrophilic CD has a bright luminescence and emission intensities that changed with the wavelength of the excitation. UV lamp analysis showed a sky blue with an absorbance value of the UV-Visible spectrum of 205 nm and an excitation wavelength of 322 nm. PL spectrum of CD shows an excitation wavelength of 460 nm. It is likely because most particles are excited at this wavelength. FTIR analysis shows that the extracted CD has carbonyl, carboxyl, and hydroxyl functional groups, which is why CD is water-soluble. HRTEM analysis shows an average particle size of 4 nm. Based on the characterization results, the excellent properties of CD made through a simple hydrothermal process make them a suitable replacement for semiconductor quantum dots, which are less popular because they are hard to make and use harsh chemicals.

Acknowledgements

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