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Study on Utilizing Oil Palm Empty Fruit Bunch Waste into Carbon Nanodots

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A B S T R A C T

This investigation introduces a proficient synthesis of carbon nanodots (CND) utilizing empty fruit bunches (EFB) as an environmentally friendly and economical carbon precursor. The synthesis method involves a combination of pyrolysis and hydrothermal. The optical and physicochemical properties of CND were investigated through X-ray diffraction (XRD), Fourier Transform Infrared (FTIR), Transmission Electron Microscopy (TEM), Particle Size Analysis (PSA), UV-visible, and fluorescence spectroscopy. The CND exhibit a spherical morphology, as confirmed through TEM imaging, with an amorphous structure. Size distribution analysis reveals a predominant particle size range between 3.8 and 4.8 nm, and an average diameter of 4.5 nm. Additionally, these CND demonstrated excellent aqueous dispersibility and exhibited fluorescence emission dependent on excitation. The synthesis procedure utilized a simple method, efficiently converting waste materials into valuable end products.

Keyword: CND, EFB, fluorescence, hydrothermal, pyrolysis.

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INTRODUCTION

Palm oil waste refers to the residues generated from the cultivation of oil palm plants, the processing of fresh fruit bunches (FFB) into crude palm oil (CPO) in palm oil mills, and the processing of kernels into palm kernel oil (PKO). After harvesting FFB, a significant amount of waste is produced annually, including empty fruit bunches (EFB), mesocarp fiber (MF), palm kernel shell or shell fractions (PS), oil palm leaves (OPL), and oil palm trunks (OPT) (Ahmad et al., 2016; Loh, 2016). EFB is one of the most abundant palm oil mills wastes. For every 1 ton of FFB processed, 22–23% or approximately 220–230 kg of EFB is produced (Fredina, 2018).

So far, the utilization of solid palm oil waste for generating new energy has been limited to its use as solid fuel for boilers. Specifically, for EFB waste, its use as boiler fuel faces constraints, including a high moisture content of 60% and the resulting pollution. Empty fruit bunch waste has not yet been utilized as an energy source, leading to the problem of an excessive accumulation of waste in areas surrounding palm oil processing industries (Surjosatyo, 2004).

EFB waste has not been effectively utilized by most palm oil mills and communities. Yet, EFB holds significant potential for conversion into carbon-based materials, as it contains 36.81% cellulose, 27.01% hemicellulose, and 15.07% lignin (Alan et al., 2022). Therefore, this study aims to utilize EFB to produce carbon nanodots (CND), which can be applied across various fields. CND are carbon-based nanomaterials with sizes <10 nm that have garnered attention due to their high-water solubility, stability, low toxicity, ease of surface modification, and simple synthesis methods. These advantages enable CND applications in bioimaging, photocatalysis, light-emitting devices, biosensing, energy conversion, and energy storage (Alas et al., 2020; Pratidhina et al., 2021).

This study explores a novel approach to synthesizing CND from EFB waste, utilizing a combination of pyrolysis and hydrothermal techniques. Two distinct synthesis methods are compared the direct carbonation of EFB and the carbonation of cellulose isolated from EFB. The research aims to develop an optimized process for producing CND with enhanced properties, suitable for a wide range of applications. By utilizing EFB, this study not only provides an environmentally friendly solution to waste management but also advances sustainable nanomaterial synthesis technologies. Notably, this investigation addresses a critical research gap, as previous studies have not extensively examined the potential of EFB as a precursor for CND synthesis using these approaches. The findings are expected to contribute significantly to the fields of sustainable material science and nanotechnology.

METHODS

Materials

The materials and their specifications used in this study were empty fruit bunches (EFB) taken from an abandoned palm oil farming (Kolaka, Indonesia) and distilled water.

Pyrolysis of EFB

In this study, EFB raw materials up to 400 g were employed in accordance with the pyrolysis reactor's capacity. Pre-treated pyrolysis raw materials, subjected to enumeration and drying, were introduced into the reactor. Pyrolysis procedures were executed at a temperature of 300 °C for 2 h with a heating rate of 10 °C per minute. The final outcomes comprised biochar and bio-oil.

Synthesis of Carbon nanodot (CND)

Biochar, weighing 5 g, was combined with 30 mL of distilled water. The resulting mixture was then transferred into a 50 mL Teflon-lined autoclave and subjected to heating at 160 °C for a duration of 4 h in an oven. The CND solution was acquired by eliminating unreacted ashes through centrifugation at 8000 rpm for 15 min. The initially prepared dark brown solution underwent additional purification via a 0.22 μm membrane filter.

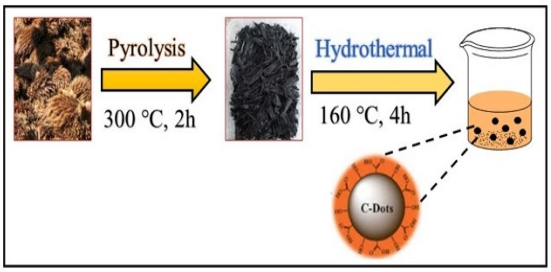


Figure 1. Processing diagram for the synthesis of CND

Carbon nanodots Characterization

Transmission electron microscopy (TEM HT7700) was operated at 80 kV to confirm the morphological characteristics of the CND. The particle size distribution was assessed at room temperature (25 °C) using the Malvern Particle Size Analyzer, with a count rate of 46.7 kcps and a 1-minute analysis period. The UV-Vis absorption spectrum and the photoluminescence spectrum were obtained with a HITACHI Y-2009 spectrometer and a PERKIN ELMER LS 4 fluorescence spectrophotometer. Fourier transform infrared (FTIR, 8400S Shimadzu) was employed to identify the bonds and functional groups on the surface of CND. X-ray diffractometer (XRD, Philips Xpert MPD, Cu Kα, λ = 1,5406 Å) was applied to determine the crystallinity of CND.

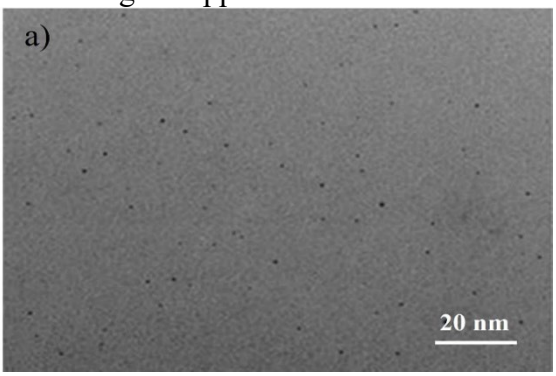
RESULTS AND DISCUSSION

Size and Morphology of CND

CND are generally three-dimensional clusters with a spherical-like structure composed of carbon atoms and tiny amounts of molecules. The inner parts of the three-dimensional clusters contain mainly sp^3 hybridization carbon atoms and a small portion of sp^2 hybridization carbon atoms. The crystal lattices of CND are well consistent with those of amorphous carbon and graphite. CND usually have a particle size of less than 10 nm, and therefore exhibit “quantum size effect”. When the particle size of CND increases, their maximal fluorescent emission wavelengths show a red-shift (Kang et al., 2020). CND mainly contain elements of C, H, O and N. The proportions of these elements are different for CND prepared by different synthetic methods.

The characterization results using TEM provide crucial information about the morphology and structure of the synthesized CND. Based on TEM analysis, the CND exhibited a spherical morphology with uniform particle distribution (see Fig. 1a). This confirms the success of the synthesis method in producing nanoparticles with consistent shapes.

The corresponding size distribution histogram is plotted in Fig. 1b, from which majority particle size distributed between 3.8 and 4.8 nm is observed, and average diameter is calculated to be 4.5 nm. These findings indicate that the synthesis process effectively produced nanoparticles with controlled sizes, a critical factor in optical and biological applications.



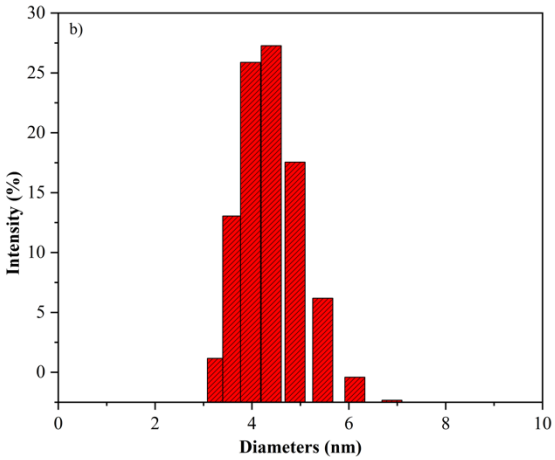


Figure 2. (a) TEM Image and (b) the particle size distribution histogram of CND.

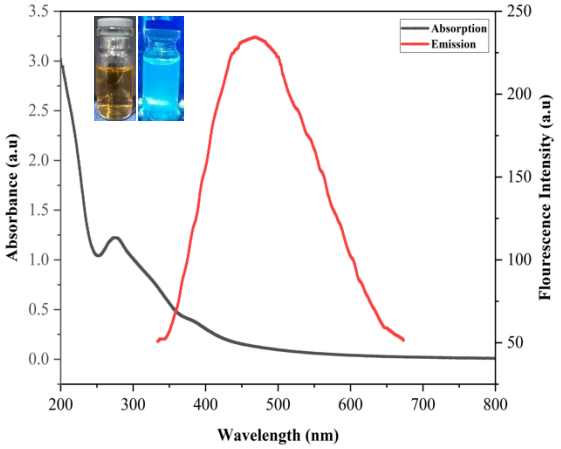


Figure 3. Absorption and fluorescence emission spectra of CND, inset: photographs CND aqueous solutions exposed to daylight (left) and 360 nm UV radiation (right).

Optical Properties of CND

The optical properties of CND were observed such as UV-visible and photoluminescence spectral studies. CND aqueous solution is pale yellow colored and transparent under daylight, while it emits bright blue fluorescence under UV light, which could be easily observed with naked eyes (insert of Fig.3) and displays an excellent aqueous dispersibility. Fig. 3 shows the UV-Vis absorption (black line) and photoluminescence (PL) spectra (red line) of as-prepared CND. From CND dispersion, an absorption peak centered at 280 nm is observed, and a strong PL emission peak centered at 465 nm is recorded under excitation at 380 nm. In the absorption spectrum, a peak at 280 nm and a hump around 370 nm characteristic for aromatic $\pi - \pi^*$ and carbonyl $n - \pi^*$ transitions respectively (Bandi et al., 2016), were observed with absorption tail extending to the visible region. The emission spectra of CND showed a strong emission peak at about 465 nm (λex = 380 nm) with a full width at half maximum (FWHM) of 87 nm which is consistent with previous reports (Xu et al., 2015; Zhang et al., 2013) and further confirms their narrow size distribution

Fourier Transform Infrared (FTIR)

FTIR spectrometer is employed to characterize CND. FTIR spectra (Fig. 4) were used to identify the surface functional groups present on EFB and CND. The FTIR spectra of EFB exhibited a broad peak at 3410 cm^{-1}, which was dominated by the stretching vibration of -OH groups whereas the peak at 2880 cm^{-1} and 2910 cm^{-1} were related to the C-H stretching vibration (Gan et al., 2020). The peak at 1541 cm^{-1} in the spectra of EFB was associated with C=C aromatic vibration from the present of lignin (Rosa et al., 2012). The band at 1740 cm^{-1} was associated with C=O stretching from hemicelluloses (Nuruddin et al., 2011).

As seen in Fig. 4, the CND obtained exhibited strong peaks at 3200 cm^{-1} and 3441 cm^{-1} represent the stretching vibration of N-H and O-H. The characteristic peaks between 2800 cm^{-1} and 3000 cm^{-1} indicate C-H stretching (Qi et al., 2019). The peaks at 1641 cm^{-1} and 1581 cm^{-1} are consistent with the bending vibration of the CO-NH group (Madrakian et al., 2017). The characteristic peaks at 1448, 1767, 1136, and 1033 cm^{-1} are attributed to C-N, C=O, C-O-C, and C-O, respectively (Su et al., 2018).

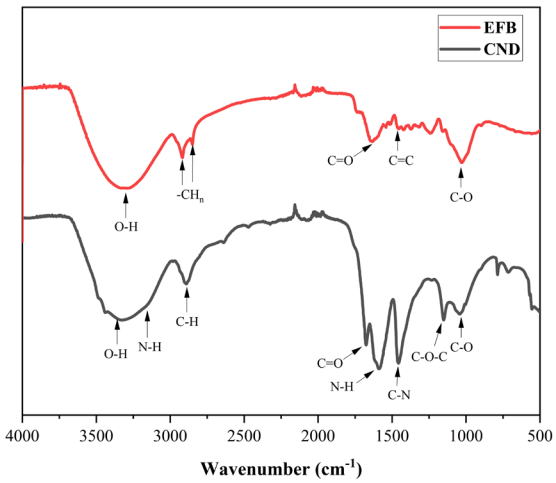


Figure 4. FTIR spectrum of EFB and CND

X-Ray Diffraction (XRD)

Fig. 5 shows the diffractogram of EFB and CND. The X-Ray Diffraction (XRD) pattern of EFB reveals broad peak at around 2θ = 22.6° which allocated to the (200) diffraction of amorphous lignocellulosic (Soom et al., 2009). The broad peak appeared at 2θ = 24° which allocated to the 002 diffraction patterns of graphitic carbon. Interlayer spacing determined from the (002) peak corresponds to d_{002} = 0.34 nm which is comparable to those previously documented carbon nanodots (Amjad et al., 2019). The small peak appeared at 2θ = 44° corresponding to the (101) plane originated due to the in-plane diffraction of graphene-like structured CND (Jones et al., 2017).

CONCLUSIONS

This study successfully developed a method for synthesizing CND using empty EFB as an environmentally friendly and economical carbon precursor. The synthesis process involved a combination of pyrolysis and hydrothermal methods. The characterization of CND revealed spherical morphology with an amorphous structure, a predominant particle size range of 3.8–4.8 nm, and an average diameter of 4.5 nm. Furthermore, the CND exhibited high aqueous dispersibility and fluorescence emission dependent on excitation. This method demonstrates high efficiency in converting waste materials into high-value products through a simple process.

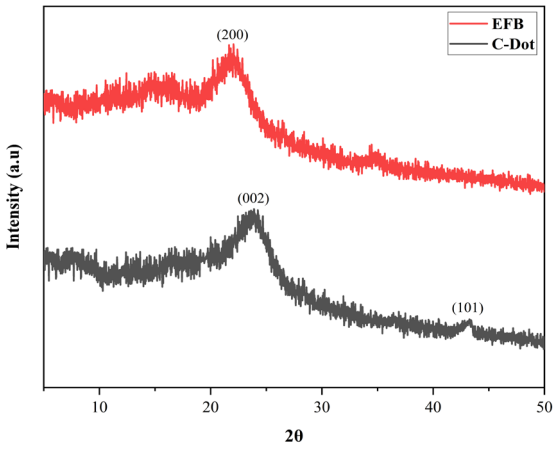


Figure 5. XRD diffractogram of EFB and CND

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