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Original Research Article

Synthesis and characterization nitrogen-doped carbon dots from candlenut shells using hydrothermal and solvothermal methods

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ABSTRACT

Candlenut shells can be utilized as precursors for Carbon Dots (CDs) since new nanoscale materials have been proven using lignin, cellulose, hemicellulose, and carbon present in candlenut shells. A carbon substance smaller than 10 nm in size, CDs have special optical properties. This research focuses on the synthesis of CDs and Nitrogen Carbon Dot (NCDs) from hazelnut shell using urea passivation agent by hydrothermal and solvothermal methods, to determine the effect of solvent on the emission produced by CDs and NCDs. Hazelnut shell was carbonized at 300°C for 6 hours. The synthesis of CDs and NCDs was carried out at 220°C for 8 hours, then sonicated at 75°C for 30 minutes. The synthesis results were centrifuged at 5000 rpm for 30 minutes, filtered using Whatman No.42 filter paper. Analysis with a 365 nm UV lamp produced bluish green luminescence, brighter luminescence was shown in NCDs by solvothermal method. UV-Vis spectra showed absorbance peaks of 289-309 nm for CDs and 335-350 nm for NCDs. FTIR spectra of CDs and NCDs produced OH, CH, C=C, C=O, C-N, CO, and C-O-C functional groups. Photoluminescence analysis showed emission peaks of CDs and NCDs at 494 nm and 496 nm for hydrothermal method, for solvothermal method at 418 nm and 432 nm. CDs and NCDs with hydrothermal method showed higher intensity than with solvothermal method. The quantum yield values obtained were 11.4226% and 25.7419% and 10.2555% and 11.7473% for hydrothermal and solvothermal methods, respectively. Solvothermal method was effective for the synthesis of CDs and NCDs with brighter luminescence.

Introduction

Carbon dots (CDs) are one type of carbon-based nanomaterial that exhibits potential. Because of their low toxicity, high solubility, and biocompatibility, CDs made of hydroxyl, carbonyl, carboxyl, and epoxy have demonstrated special and advantageous properties that could replace semiconductor quantum dots and organic dyes. These properties allow for a wide range of applications, including bioimaging, drug delivery via nanocarriers, medical diagnostics, analyte detection, metal detection, and photocatalysts (Liu et al., 2020). The rapid development of nanotechnology has allowed researchers to produce a vast array of nanomaterials with a wide variety of uses (Zhou et al., 2019; Magesa et al., 2020). CDs are quasi-spherical, submicron-sized nanoparticles. CDs have many unique advantages, including as high water solubility, robust cell permeability, sensitive surface modification, great photoluminescence capabilities, minimal toxicity, and an abundant supply of raw ingredients (Ghosal & Ghosh, 2019; Chung et al., 2020; Marpongahtun et al., 2023).

Organic waste from agriculture has not received much attention, but it could be a potential source of carbon. Therefore, there is a great opportunity to employ this trash as the main component in the CDs-making process. Because carbon sources from natural materials are abundant, environmentally friendly, and effective as sources of raw materials for products like cellulose, hemicellulose, lignin, proteins, and carbohydrates, researchers have concentrated a lot of effort on using them to synthesize CDs (Dong et al., 2013). The basic building blocks of CDs are carbon chains and carbon compounds. Natural materials come in a wide variety and can be used as carbon sources. Until now, a wide variety of organic foods have been used as carbon sources in the production of CDs (Bhattacharya et al., 2022).

Aleurites moluccana, or candlenut shell, is one of the precursors that can be used in the CDs-making process. The by-product of processing candlenut seeds is candlenut shell. Only a small portion of people really use candlenut shells, and most are squandered. A candlenut shell has the following percentages: lignin (13.79%), cellulose (27.14%), and hemicellulose (48.47%, the most common form) (Salindeho, 2017). Researchers have concentrated a lot of attention on carbon sources from natural materials for the synthesis of CDs because they are abundant, environmentally friendly, efficient, and renewable

sources of raw materials such as cellulose, hemicellulose, lignin, carbohydrates, and proteins (Kang et al., 2020). The main component of CDs are carbon chains, sometimes referred to as carbon compounds, which are present in a wide range of natural materials (Hulupi et al., 2022). Previous studies have created CDs from a variety of biomasses, including oil palm empty fruit bunches (Marpongahtun et al., 2018; Pramudita et al., 2022), jengkol skin (Prayugo et al., 2023), star fruit (Piliang et al., 2022), and soybean (Ayu et al., 2023). Among the different biomass materials that have been employed, no one has yet used biomass obtained from candlenut shells. Candlenut shells are hence the forerunner of CDs used in this study.

Biomass-based CDs are low yielding and luminescent. To improve their fluorescence properties, CDs are commonly surface passivated and doped with heteroatoms. Metal atom doping is costly and hazardous, and surface passivation is a time-consuming and intricate procedure. In contrast, due to their low cost and low toxicity, doping nonmetallic elements, such as nitrogen, turns into an efficient and cost-effective approach. Even though the exact process underlying CDs' fluorescence release is still unknown, nitrogen atoms, which are the same size as carbon atoms, can interact with their five valence electrons to effectively manage the intrinsic properties of CDs and increase fluorescence (Ge et al., 2022).

Several functional groups, including -COOH, -OH, and -NH_2, are present on the surface of CDs (Kou et al., 2020). Specifically, it has been shown that a higher concentration of functional groups on the surface of CDs increases the intensity of their luminescence (Liang et al., 2019). The emission of CDs is also affected by passivation agents. Because these passivation agents are composed of functional groups containing atoms of nitrogen and sulfur, they can increase the luminescence and solubility of CDs (Dong et al., 2013). CDs can have heteroatoms such as boron, sulfur, or nitrogen added to their structure to change their optical properties and increase their conductivity or fluorescence. The sp2 carbon core of CDs is the source of their fluorescence (Li et al., 2019), and heteroatom dopants may provide sp2 hybridization sites, making them a useful tool for modifying the fluorescence properties of CDs (Kou et al., 2020). Heteroatom dopants have the potential to increase the quantum yield, fluorescence intensity, and high conversion characteristics of CDs by causing extra surface defects to occur and a reduction in the energy between band gaps (Manioudakis et al., 2019; Park et al., 2020; Liu et al., 2023).

A wide range of methods may be utilized to create CDs, including as hydrothermal, solvothermal chemical ablation, electrochemical carbonization, arc discharge, laser ablation, and microwave irradiation (Ghosal & Ghosh, 2019). Most of the methods require the use of specialized equipment, catalysts, and dangerous solvents. However, solvothermal and hydrothermal methods are simple and safe for the environment (Ji et al., 2020). When employing the hydrothermal technique, chemical reactions occur in a confined space with high temperatures and high pressures as well as in water. On the other hand, it uses organic solvents instead of water. On the other hand, the hydrothermal technique is improved upon by the solvothermal approach (Xu et al., 2018). The choice of organic solvent may have an impact on the emission produced during CDs synthesis when employing the solvothermal technique. In particular, the solvothermal technique is the most feasible and cost-effective method of producing CDs from dye-containing materials (Ding et al., 2017).

In this study, the precursor used was derived from candlenut shells. This research focuses on the synthesis of carbon dots (CDs) and nitrogen carbon dot (NCDs) from candlenut shells using urea passivation agent by hydrothermal and solvothermal methods. The solvents used are deionized water and methanol. This was done to determine the effect of solvent on the emission produced by CDs and NCDs using hydrothermal and solvothermal methods. Furthermore, CDs and NCDs were characterized using ultraviolet (UV) lamp, ultraviolet-visible (UV-Vis) spectrophotometer, Fourier Transform Infrared (FTIR) spectrophotometer, and Photoluminisensi (PL) spectroscopy.

Methods

Materials

The materials used in this study are: Candlenut shell, Aquadest, Deionized water (Merck), Methanol (Merck), Urea (Merck). The tools used in the research are: Glassware (Pyrex), Analytical Balance (Toledo), Hot plate (Cimarex), Magnetic stirrer (Merck), Autoclave (Biobase BKM P-18 (A)), UV lamp (Panasonic), Centrifugation (MPW MED Instrument), Furnace (Bio-One), Blender (Panasonic), Filter paper (Wattman No. 42), Oven (Bio-One). 42), Oven (Bio-One), Ultrasonic Bath (Elmasonic E-15H), UV-Vis spectrophotometer (Shimadzu), Fourier Transformation Infrared (FTIR) spectrophotometer (Shimadzu IR Prestige21), Photoluminisensi (PL) spectroscopy (Horiba FL 1000).

Preparation Sample

Candlenut shells were washed thoroughly to remove impurities and then dried in the sun for 3 days, then incinerated at 300˚C for 6 hours to produce candlenut shell carbon (Pramudita et al., 2022).

Synthesis of Carbon Dots

A total of 10 g of candlenut shell carbon was dispersed into 50 mL of deionized water (or Methanol) and stirred using a magnetic stirrer for 30 minutes to obtain a well-dispersed candlenut shell aqueous solution. Then transferred into a 100 mL Teflon-coated stainless steel autoclave and heated at 220˚C for 8 hours. After cooling to room temperature, the suspension was ultrasonicated, followed by centrifugation at 5,000 rpm for 30 minutes and then filtered with Whatman no. 42 filter paper. The successfully synthesized CDs were characterized using UV lamp, UV-Vis, FTIR, and PL (Zhang et al., 2022). The same procedure was carried out for the synthesis of NCDs with the addition of urea passivation agent.

Characterization of Carbon Dots

UV Lamp

The resulting CDs and NCDs solutions were put into test tubes and then irradiated under a UV lamp for fluorescence color analysis.

UV-Vis Characterization

CDs and NCDs solutions of 10 mL each were characterized using UV-Vis to analyze the transition or excitation of the core state (π-π*) and surface state (n-π*). The process was carried out using UV-Vis spectroscopic absorption at a wavelength of 200-800 nm.

Fourier Transformation Infrared (FTIR) Characterization

CDs and NCDs solutions of 10 mL were characterized using FTIR analysis to detect the functional groups formed in CDs and NCDs from candlenut shells with a wavelength range of 4500-450 cm^{-1}.

Photoluminescent (PL) Characterization

CDs and NCDs solutions of 10 mL each were characterized using photoluminescence analysis to determine the wavelength emission using a spectrophotometer with a wavelength of 400-900 nm. The Quantum Yield calculation was then carried out using floro tools software. Quantum Yield values of CDs and NCDs with hydrothermal and solvothermal methods can be calculated using Equation:

$$QYc = QYs \times \frac{Ic}{Is} \times \frac{As}{Ac} \times \left(\frac{\eta c}{\eta s}\right)^2$$

Description:

QYc = Quantum yield CDs
QYs = Quantum yield Reference (quinine sulfate)
Ic = CDs integral fluorescence peak area
Is = Reference integral fluorescence peak area (quinine sulfate)
As = Absorbance Reference (quinine sulfate)
Ac = Absorbance CDs
η_c = Refractive index of CDs
η_s = Refractive index of Reference (quinine sulfate)

Results and Discussion

There were multiple phases involved in the synthesis of CDs and NCDs. The initial phase involved heating candlenut shells in a furnace to create a carbon matrix, which was then used to build CDs and NCDs using solvothermal and hydrothermal techniques derived from the precursor carbon matrix. In the last stage, the synthesized CDs and NCDs were characterized using ultraviolet (UV) lamp, ultraviolet-visible (UV-Vis) spectrophotometer, Fourier Transform Infrared (FTIR) spectrophotometer, and Photoluminisensi (PL) spectroscopy.

Preparation Sample

Candlenut shells were processed via a number of steps to provide the material needed to make Carbon Dots. The first step in sample preparation was to wash the candlenuts with distilled water to remove any impurities that could have adhered to the sample. After cleaning, the sample was left to dry in the sun for three days. The dried candlenut shell samples were torched in a furnace for six hours at 300 degrees Celsius to produce a carbon matrix made of candlenut shells. Additionally, CDs and NCDs were synthesized at certain pressures and temperatures using solvothermal and hydrothermal methods.

Synthesis of Carbon Dots

Using solvents like methanol and deionized water, carbon dots were created by hydrothermal and solvothermal methods. Using urea as a passivation agent modifies the surface structure of CDs. After dissolving 10 g of carbon matrix prepared from candlenut shells in methanol or deionized water and heating it to 220°C for eight hours, urea was used as a source of nitrogen (N). The procedure was repeated with the addition of urea as a passivation agent. Characterizing the synthesized CDs and NCDs was done using the UV light, UV-Vis, FTIR, and PL. Illustration of CDs and NCDs synthesis using hydrothermal and solvothermal methods is shown in Fig-1.

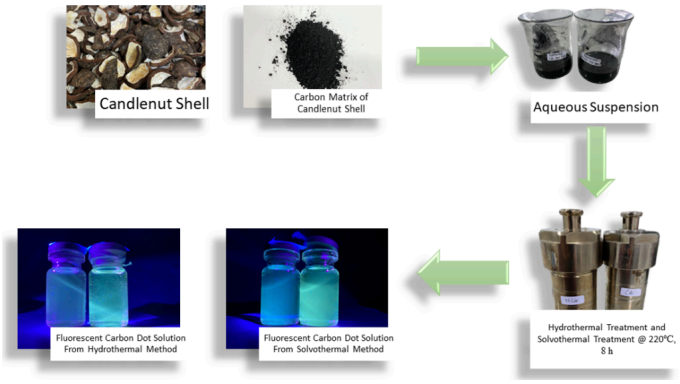

Fig-1. Synthesis of CDs and NCDs from candlenut shells using hydrothermal and solvothermal methods.

Characterization of Carbon Dots

UV Lamp

The produced CDs and NCDs had bluish-green fluorescence, as measured by UV light examination at a wavelength of 365 nm. The carbon nuclei in the precursor source, which were obtained from the functional groups of natural compounds, produced this light. Furthermore, there was no sign of degradation or precipitation in the samples, and the CDs and NCDs continued to glow for several weeks. The fluorescence of carbon dots can be seen in Fig-2b and Fig-2d.

(a) (b) (c) (d)

Fig-2. (a) CDs and NCDs under light in hydrothermal process; (b) CDs and NCDs under 365 nm UV lamp in hydrothermal process; (c) CDs and NCDs under light in solvothermal process; and (d) CDs and NCDs under 365 nm UV lamp in solvothermal process.

It is possible to see specific luminescence variations between CDs and NCDs produced using solvothermal and hydrothermal processes. The solvothermal technique produces CDs and NCDs with higher luminescence when methanol solvent is used. Methanol is an organic solvent that may attach to the precursor nucleus, slowing down crystal formation and stabilizing smaller crystals (Bang & Suslick, 2010). The luminescence under a 365 nm UV light enhanced when urea was added to the CD formulation as a passivation agent. This finding is in line with other studies that show how the use of passivation agents may increase luminescence intensity by enhancing the surface area of CDs with more functional groups (Ding et al., 2020). The solutions of CDs and NCDs observed under visible light and 365 nm UV light are shown in Fig-2.

UV-Vis

To confirm the synthesis of carbon dots, the sample's absorption pattern may be analyzed and the absorbance of the CDs material can be measured using a UV-Vis spectrophotometer operating in the 200–800 nm wavelength range. CDs frequently have a characteristic absorption peak in the UV-Vis band, which ranges from 220 to 480 nm (Jiang et al., 2019). The synthesized CDs and NCDs for both approaches exhibited a bluish-green color, as seen in Fig-2, Fig-2b, and Fig-2d. The absorbance pattern of CDs and NCDs from candlenut shell was analyzed using a hydrothermal method, which showed absorbance peaks at wavelengths of 289 nm and 348 nm for CDs and 290 nm and 350 nm for NCDs. NCDs employed the hydrothermal technique to obtain the highest intensity. Utilizing the solvothermal approach, the absorbance pattern for CDs and NCDs from candlenut shell revealed absorbance peaks at wavelengths of 295 nm and 335 nm for CDs and 309 nm and 350 nm for NCDs. Candlenut shell-derived CDs and NCDs had an absorbance of 289–309 nm. The peak shows the absorbance of the π-π* electron transition from the sp2 hybridization bond's carbonization and the n-$\pi*$ from the C=O group and nitrogen-containing compounds. The use of passivation agents caused the absorption wavelength to move into the visible light range of 335, 348, 350, and 350 nm. This is because the surface of CDs contains amine groups (Wang et al., 2020). The amine group serves as an excited electron trap or an electron trapping site; the light absorbance increases with the number of trapped electrons (Zhang et al., 2021). It is also proposed that the rise in absorbance wavelength at 350 mm is due to the creation of an energy level called the trapping of excited state, which may absorb photon energy with wavelengths in the visible area. According to Saengsrichan et al. (2022), Fig-3 illustrates how this leads to a broader absorption of light. It is likely that the different spectral patterns observed in UV-Vis spectra are due to the use of different solvents that produce different functional groups on the surface of CDs and NCDs. Peak broadening between the synthesized CDs and NCDs may happen as a result of their different sizes, which cause variations in the wavelength of emitted fluorescence (Yang et al., 2008).

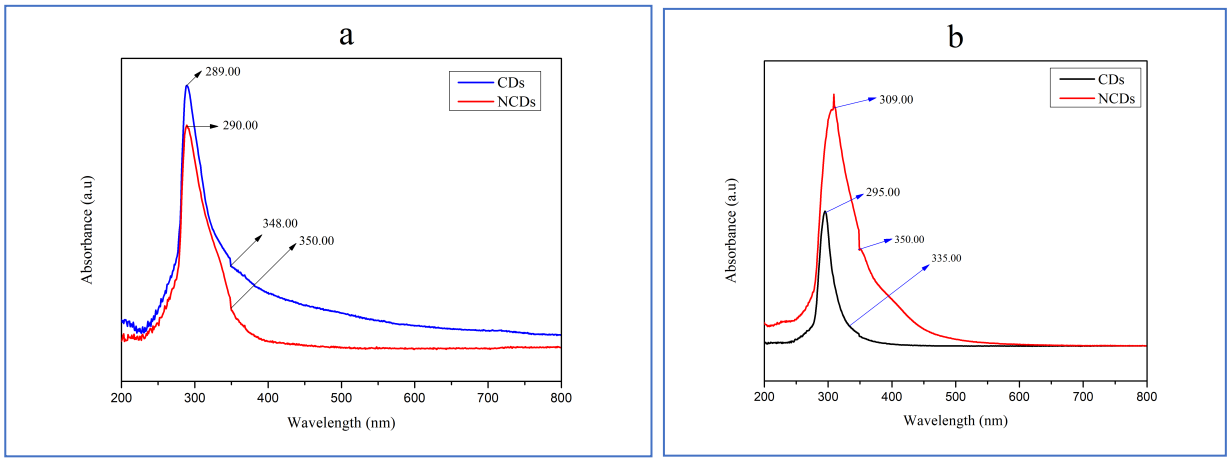

Fig-3. UV-Vis spectra of CDs and NCDs. a: Hydrothermal method; b: Solvothermal method.

The variation in carbon dot energy levels both before and after nitrogen doping is responsible for the shift in the maximum absorbance length of CDs and NCDs, which can impact the absorbance and emission characteristics. Because the surface functional groups and the condition of the produced carbon nucleus during the passivation process (creation of CDs surface groups) in the hydrothermal and solvothermal processes are the same, the absorption peak is independent of the urea concentration. As the concentration of urea rises, the absorption intensity usually falls off. N dopants, which are helpful in reducing the epoxy groups on the CDs surface and converting them into amides and aliphatic amines, are the cause of this. It will be more difficult for the CDs to absorb light, though, if the concentration is too high since the electron donor N will also grow and there will be an electron cloud density (Manioudakis et al., 2019). Conversely, a tiny concentration of the N passivation agent will result in small active amine groups, which will make it harder for the CDs to absorb light and affect the intensity of absorption.

FTIR

In addition to UV–Vis measurements, Fourier Transform Infrared (FTIR) spectrophotometer measurements at wave numbers 500–4000 cm-1 can be utilized to validate the success of CDs synthesis. Fig-4 shows the FTIR spectra of CDs and NCDs from candlenut shells. The absorption bands of CDs and NCDs synthesized by the hydrothermal technique show shifts in the OH peak, C=O (carbonyl) at 1630 cm-1, C=C at 1562 cm-1, N-H (amine) at 1505 cm-1, and shifts in sp3 CH and sp2 CH at 1105 cm-1 and 1017 cm-1 (Ayu et al., 2023). While CDs and NCDs synthesized by the solvothermal technique have a C-O (alcohol) shift peak at 1118 cm-1, the absorption band of NCDs exhibits a C-N shift peak at 1397 cm-1. Wave number 3325 cm-1, the OH peak shift, C=O, C=C, and N-H shifts at 1454 and 1427 cm-1, C-N at 1362 cm-1, OH at 1282 cm-1, C-O-C at 1196 cm-1, and CH at 1014 and 1059 cm-1 are all related with CH sp3 groups from methanol. The shift peaks at 1655 cm-1 as well. The FTIR spectra of CDs and NCDs vary in that the existence of a C-N shift in NCDs proves the efficacy of nitrogen modification on the surface structure, which is consistent with the findings reported by Amrina Rosyada with precursor Kesumba Keling seeds and pods (Rosyada et al., 2023).

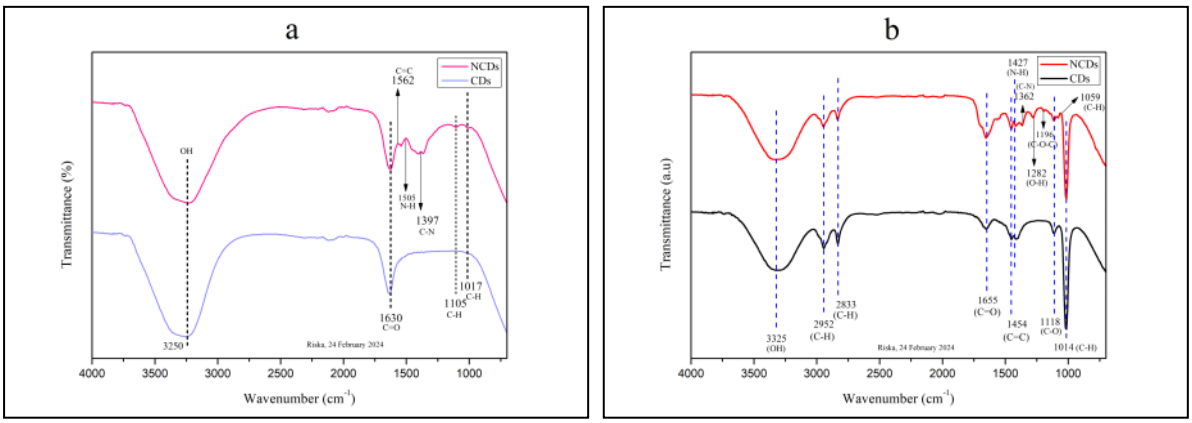

Fig-4. FTIR spectra of CDs and NCDs. a: Hydrothermal method; b: Solvothermal method.

Photoluminescent (PL)

The wavelength of light emission resulting from stimulation may be measured using a fluorescence spectrophotometer (PL), which can be used to evaluate CD samples and provide a spectrum and luminescence intensity. The synthesis of CDs may also be confirmed using this technique. As shown in Fig-5, every CD sample used in this study was stimulated at 365 nm. In general, three parameters affect the PL properties of CDs: (1) gap energy (Eg); (2) surface groups in the CDs structure; and (3) CDs quantum particle size (Sarkar et al., 2016). CDs from hazelnut shells have an excitation peak of 395 mm and an emission peak of 494 nm when employing the hydrothermal process, according to the fluorescence spectrum's properties. In the meantime, the solvothermal method's CD emission peak was measured to be at 418 nm in wavelength. Every sample has the same excitation wavelength of 395 nm. The emission characteristics of CDs at a wavelength of 450-550 nm, which includes the green emission area, can be deduced from the presence of sp2 bonds, surface groups, and defects in their emission structure. It is possible to attribute the significant CD emission in the visible light band (>400 nm) to the existence of heterogeneous groups in the CDs structure (Prasannan & Imae, 2013).

Table. 1 QY CDs and NCDs values of hydrothermal and solvothermal methods.

No	Materials	λExcitation	λEmission	QY (%)
1	CDs (hydrothermal method)	365 nm	494 nm	11.4226
2	NCDs (hydrothermal method)	365 nm	496 nm	25.7419
3	CDs (solvothermal method)	365 nm	418 nm	10.2555
4	NCDs (solvothermal method)	365 nm	432 nm	11.7473
5	Quinine sulphat	350 nm	550 nm	0.5400

The presence of N dopants on CDs can result in heteroatom groups. Surface passivation is the term for the flaws caused by N doping in the surface structure of CDs. The heteroatom groups created by this surface passivation technique will have an effect on photoluminescence emission because they function as traps or electron acceptors from bond excitation (Xu et al., 2017). The formation of C-N groups and increased absorbance on urea-doped CDs produced by these results are in line with the examination of FTIR and UV-Vis data in the preceding subchapter. Figure 6 shows a decrease in fluorescence intensity

and an increase in emission wavelength, indicating that the addition of urea dopant can inhibit or prevent electron-hole recombination, resulting in an increase in the deprotonation process or H+ formation (Liu et al., 2021).

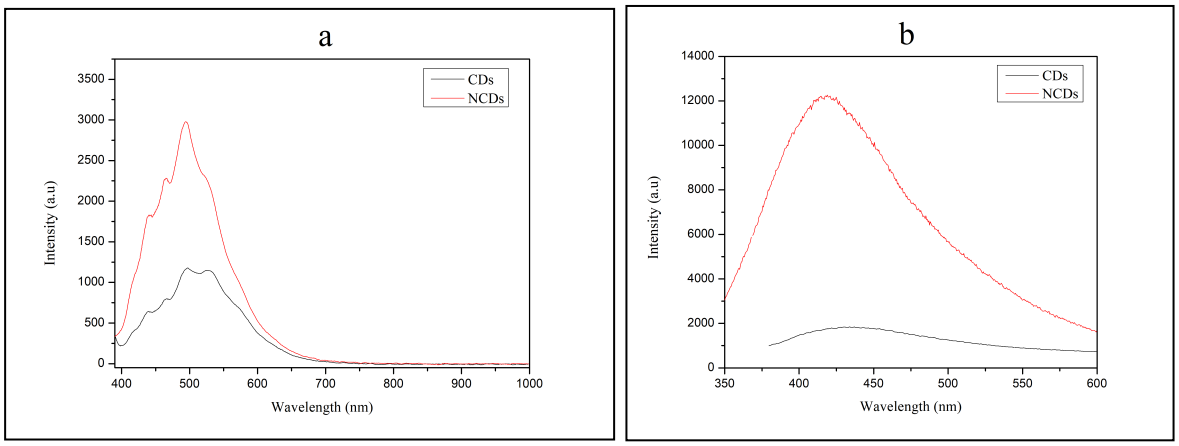

Fig-5. Photoluminescent spectra of CDs and NCDs. a: Hyrothermal method, b: Solvothermal method.

A standard solution of quinine sulfate 0.54 M H_2SO_4 at an excitation wavelength of 350 nm was used as a reference for the Quantum Yield CDs calculation, which was performed using the Tecan method on the Floro Tools program (Prathumsuwan et al., 2018). In this study, the QY CDs values of candlenut shells were 11.4226%, 25.7419%, 10.2555%, and 11.7473%, respectively, as shown in Table 1.

As the fluorescence wavelength of CDs increases, QY steadily decreases; the most critical factors are associated with various techniques, synthesis procedures, and extraction conditions (Lima et al., 2013), Heteroatom groupings induce structural changes in CDs through photon induction on various functional groups on the structure's surface (Longo et al., 2020). Urea addition has an inverse relationship with QY and a direct relationship with fluorescence emission. Agglomeration, the aggregation of "dot" particles that causes changes in CD structure, is triggered by the injection of a high concentration of urea passivation agent. Agglomeration disrupts photon induction, which lowers the QY value (Longo et al., 2020).

Conclusion

CDs and NCDs were successfully synthesized from candlenut shells using hydrothermal and solvothermal methods. The solvothermal method produced a brighter bluish-green luminescence than the hydrothermal method. UV-Vis spectra showed absorbance peaks of 289-309 nm for CDs and 335-350 nm for NCDs. FTIR spectra of CDs and NCDs produced OH, CH, C=C, C=O, C-N, CO, and C-O-C functional groups. Photoluminescence analysis showed emission peaks of CDs and NCDs at 494 nm and 496 nm with the hydrothermal method, and at 418 nm and 432 nm with the solvothermal method. The intensity of CDs and NCDs with the hydrothermal method shows higher intensity. The quantum yeild values of CDs and NCDs obtained from the hydrothermal and solvothermal methods were 11.4226% and 25.7419% and 10.2555% and 11.7473%, respectively. The solvothermal method is effective for the synthesis of CDs and NCDs with brighter luminescence.

Conflict of Interests

The author(s) declares that there is no conflict of interest in this research and manuscript.

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References

Ayu, D. G., Gea, S., Andriayani, N., Telaumbanua, D. J., Piliang, A. F. R., Harahap, M., Yen, Z., Goei, R., & Tok, A. I. Y. (2023). Photocatalytic degradation of methylene blue using N-Doped ZnO/Carbon Dot (N-ZnO/CD) nanocomposites derived from organic soybean. *ACS Omega*, 8(17), 14965–14984. https://doi.org/10.1021/acsomega.2c07546

Bang, J. H., & Suslick, K. S. (2010). Applications of ultrasound to the synthesis of nanostructured materials. *Advanced Materials*, 22(10), 1039–1059. https://doi.org/10.1002/adma.200904093

Bhattacharya, D., Kumar, V., & Packirisamy, G. (2022). Biocompatible carbon nanodots from red onion peels for anti-oxidative and bioimaging applications. *Materials Express*, 11(12), 1958–1965. https://doi.org/10.1166/mex.2021.2101

Chung, Y. J., Kim, J., & Park, C. B. (2020). Photonic Carbon Dots as an Emerging Nanoagent for Biomedical and Healthcare Applications. *ACS Nano*, 14(6), 6470–6497. https://doi.org/10.1021/acsnano.0c02114

Ding, H., Ji, Y., Wei, J. S., Gao, Q. Y., Zhou, Z. Y., & Xiong, H. M. (2017). Facile synthesis of red-emitting carbon dots from pulp-free lemon juice for bioimaging. *Journal of Materials Chemistry B*, 5(26), 5272–5277. https://doi.org/10.1039/c7tb01130j

Ding, H., Li, X. H., Chen, X. B., Wei, J. S., Li, X. B., & Xiong, H. M. (2020). Surface states of carbon dots and their influences on luminescence. *Journal of Applied Physics*, 127(23). https://doi.org/10.1063/1.5143819

Dong, Y., Pang, H., Yang, H. Bin, Guo, C., Shao, J., Chi, Y., Li, C. M., & Yu, T. (2013). Carbon-based dots co-doped with nitrogen and sulfur for high quantum yield and excitation-independent emission. *Angewandte Chemie - International Edition*, 52(30), 7800–7804. https://doi.org/10.1002/anie.201301114

Ge, G., Li, L., Chen, M., Wu, X., Yang, Y., Wang, D., Zuo, S., Zeng, Z., Xiong, W., & Guo, C. (2022). Green synthesis of nitrogen–doped carbon dots from fresh tea leaves for selective Fe3+ ions detection and cellular imaging. *Nanomaterials*, 12(6). https://doi.org/10.3390/nano12060986

Ghosal, K., & Ghosh, A. (2019). Carbon dots: The next generation platform for biomedical applications. *Materials Science and Engineering C*, 96, 887–903. https://doi.org/10.1016/j.msec.2018.11.060

Hulupi, M., Nabilah, N., Nabilah, T. H., Keryanti, K., & Abdilah, F. (2022). Sintesis carbon nanodots dari molase menggunakan metode pemanasan terbantukan gelombang mikro. *Equilibrium Journal of Chemical Engineering*, 6(1), 31–35. https://doi.org/10.20961/equilibrium.v6i1.61212

Ji, C., Zhou, Y., Leblanc, R. M., & Peng, Z. (2020). Recent developments of carbon dots in biosensing: A review. *ACS Sensors*, 5(9), 2724–2741. https://doi.org/10.1021/acssensors.0c01556

Jiang, K., Feng, X., Gao, X., Wang, Y., Cai, C., Li, Z., & Lin, H. (2019). Preparation of multicolor photoluminescent carbon dots by tuning surface states. *Nanomaterials*, 9(4), 1–12. https://doi.org/10.3390/nano9040529

Kang, C., Huang, Y., Yang, H., Yan, X. F., & Chen, Z. P. (2020). A review of carbon dots produced from biomass wastes. *Nanomaterials*, 10(11), 1–24. https://doi.org/10.3390/nano10112316

Kou, X., Jiang, S., Park, S. J., & Meng, L. Y. (2020). A review: recent advances in preparations and applications of heteroatom-doped carbon quantum dots. *In Dalton Transactions*, 49, (21). https://doi.org/10.1039/d0dt01004a

Li, F., Yang, D., & Xu, H. (2019). Non-metal-heteroatom-doped carbon dots: Synthesis and properties. *Chemistry - A European Journal*, 25(5), 1165–1176. https://doi.org/10.1002/chem.201802793

Liang, W., Li, Z., Li, H., Liu, Z., Wang, X., & Yang, K. (2019). The influence of functional group on photoluminescence properties of carbon dots. *ECS Journal of Solid State Science and Technology*, 8(12), R176–R182. https://doi.org/10.1149/2.0131912jss

Lima, N. B. D., Gonçalves, S. M. C., Júnior, S. A., & Simas, A. M. (2013). A comprehensive strategy to boost the quantum yield of luminescence of europium complexes. *Scientific Reports*, 3(Iii), 1–8. https://doi.org/10.1038/srep02395

Liu, C., Zhang, F., Hu, J., Gao, W., & Zhang, M. (2021). A mini review on pH-sensitive photoluminescence in carbon nanodots. Frontiers in Chemistry, 8(January), 1–9. https://doi.org/10.3389/fchem.2020.605028

Liu, J., Li, R., & Yang, B. (2020). Carbon Dots: A new type of carbon-based nanomaterial with wide applications. *ACS Central Science*, 6(12), 2179–2195. https://doi.org/10.1021/acscentsci.0c01306

Liu, K., Xia, C., Guo, Y., Yu, H., Xie, Y., & Yao, W. (2023). Polyethylenimine-functionalized nitrogen and sulfur co-doped carbon dots as effective fluorescent probes for detection of Hg2+ ions. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 122395. https://doi.org/10.1016/j.saa.2023.122395

Longo, A. V., Sciortino, A., Cannas, M., & Messina, F. (2020). UV photobleaching of carbon nanodots investigated by: In situ optical methods. *Physical Chemistry Chemical Physics*, 22(24), 13398–13407. https://doi.org/10.1039/d0cp00952k

Magesa, F., Wu, Y., Dong, S., Tian, Y., Li, G., Vianney, J. M., Buza, J., Liu, J., & He, Q. (2020). Electrochemical sensing fabricated with TA2O5 nanoparticle-electrochemically reduced graphene oxide nanocomposite for the detection of oxytetracycline. *Biomolecules*, 10(1), 1–13. https://doi.org/10.3390/biom10010110

Manioudakis, J., Victoria, F., Thompson, C. A., Brown, L., Movsum, M., Lucifero, R., & Naccache, R. (2019). Effects of nitrogen-doping on the photophysical properties of carbon dots. *Journal of Materials Chemistry C*, 7(4), 853–862. https://doi.org/10.1039/c8tc04821e

Marpongahtun, Andriayani, Muis, Y., Gea, S., Amaturrahim, S. A., Attaurrazaq, B., & Daulay, A. (2023). Synthesis of nitrogen-doped carbon dots from nanocrystalline cellulose by pyrolysis method as Hg2+ detector. *International Journal of Technology*, 14(1), 219–231. https://doi.org/10.14716/ijtech.v14i1.4863

Marpongahtun, Gea, S., Muis, Y., Andriayani, Novita, T., & Piliang, A. F. (2018). Synthesis of Carbon nanodots from cellulose nanocrystals oil palm empty fruit by pyrolysis method. *Journal of Physics: Conference Series*, 1120(1). https://doi.org/10.1088/1742-6596/1120/1/012071

Park, Y., Kim, Y., Chang, H., Won, S., Kim, H., & Kwon, W. (2020). Biocompatible nitrogen-doped carbon dots: synthesis, characterization, and application. *Journal of Materials Chemistry B*, 8(39), 8935–8951. https://doi.org/10.1039/d0tb01334j

Piliang, A. F. R., Tarigan, K., Humaidi, S., Barus, D. A., & Gea, S. (2022). Nitrogen-doped carbon dots from bilimbi juice (Averrhoa bilimbi L.) via hydrothermal method for iron and mercury sensing. *Elkawnie*, 8(1), 149. https://doi.org/10.22373/ekw.v8i1.11813

Pramudita, R., Marpongahtun, Gea, S., Daulay, A., Harahap, M., Tan, Y. Z., Goei, R., & Tok, A. I. Y. (2022). Synthesis of fluorescent citric acid carbon dots composites derived from empty fruit bunches of palm oil tree and its anti-bacterial property. *Case Studies in Chemical and Environmental Engineering*, 6(1), 100277. https://doi.org/10.1016/j.cscee.2022.100277

Prasannan, A., & Imae, T. (2013). One-pot synthesis of fluorescent carbon dots from orange waste peels. *Industrial and Engineering Chemistry Research*, 52(44), 15673–15678. https://doi.org/10.1021/ie402421s

Prathumsuwan, T., Jamnongsong, S., Sampattavanich, S., & Paoprasert, P. (2018). Preparation of carbon dots from succinic acid and glycerol as ferrous ion and hydrogen peroxide dual-mode sensors and for cell imaging. *Optical Materials*, 86, 517–529. https://doi.org/10.1016/j.optmat.2018.10.054

Prayugo, A. S., Marpongahtun, Gea, S., Daulay, A., Harahap, M., Siow, J., Goei, R., & Tok, A. I. Y. (2023). Highly fluorescent nitrogen-doped carbon dots derived from jengkol peels (Archindendron pauciflorum) by solvothermal synthesis for sensitive Hg2+ ions detection. *Biosensors and Bioelectronics: X*, 14(1), 100363. https://doi.org/10.1016/j.biosx.2023.100363

Rosyada, A., Sugiarti, S., & Suparto, I. H. (2023). Synthesis of Carbon Dot Nanoparticles (C-Dot) from Seeds and Seedpods of Kesumba Keling (Bixa orellana) using Hydrothermal and Solvothermal Methods. *Jurnal Kimia Sains dan Aplikas*i, 26(6), 204–210. https://ejournal.undip.ac.id/index.php/ksa/article/view/53542

Saengsrichan, A., Saikate, C., Silasana, P., Khemthong, P., Wanmolee, W., Phanthasri, J., Youngjan, S., Posoknistakul, P., Ratchahat, S., Laosiripojana, N., Wu, K. C. W., & Sakdaronnarong, C. (2022). The Role of N and S doping on photoluminescent characteristics of carbon dots from palm bunches for fluorimetric sensing of Fe3+ ion. *International Journal of Molecular Sciences*, 23(9). https://doi.org/10.3390/ijms23095001

Salindeho, N. (2017). Asap Cair Hasil Pirolisis Cangkang Pala Dan Cangkang Kemiri. In Unsrat Press (Vol. 13, Issue 1).

Sarkar, S., Banerjee, D., Ghorai, U. K., & ChattoPadhyay, K. K. (2016). Hydrothermal synthesis of carbon quantum dots and study of its photoluminecence property. *International Conference on Microelectronics, Computing and Communication, MicroCom*. https://doi.org/10.1109/MicroCom.2016.7522521

Wang, Y., Hu, X., Li, W., Huang, X., Li, Z., Zhang, W., Zhang, X., Zou, X., & Shi, J. (2020). Preparation of boron nitrogen co-doped carbon quantum dots for rapid detection of Cr(VI). *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*, 243, 118807. https://doi.org/10.1016/j.saa.2020.118807

Xu, Q. T., Li, J. C., Xue, H. G., & Guo, S. P. (2018). Binary iron sulfides as anode materials for rechargeable batteries: Crystal structures, syntheses, and electrochemical performance. *Journal of Power Sources*, 379(December 2017), 41–52. https://doi.org/10.1016/j.jpowsour.2018.01.022

Xu, S., Liu, Y., Yang, H., Zhao, K., Li, J., & Deng, A. (2017). Fluorescent nitrogen and sulfur co-doped carbon dots from casein and their applications for sensitive detection of Hg2+ and biothiols and cellular imaging. *Analytica Chimica Acta*, 964, 150–160. https://doi.org/10.1016/j.aca.2017.01.037

Yang, X. F., Liu, Z. L., Chen, P. P., Chen, X. S., Li, T. X., & Lu, W. (2008). Broadening of photoluminescence by nonhomogeneous size distribution of self-assembled InAs quantum dots. *Chinese Physics Letters*, 25(8), 3059–3062. https://doi.org/10.1088/0256-307X/25/8/087

Zhang, Q., Wang, R., Feng, B., Zhong, X., & Ostrikov, K. (Ken). (2021). Photoluminescence mechanism of carbon dots: triggering high-color-purity red fluorescence emission through edge amino protonation. *Nature Communications*, 12(1), 1–13. https://doi.org/10.1038/s41467-021-27071-4

Zhang, T., Ji, Q., Song, J., Li, H., Wang, X., Shi, H., Niu, M., Chu, T., Zhang, F., & Guo, Y. (2022). Preparation of nitrogen and sulfur co-doped fluorescent carbon dots from cellulose nanocrystals as a sensor for the detection of rutin. *Molecules*, 27(22). https://doi.org/10.3390/molecules27228021

Zhou, Y., Mintz, K. J., Sharma, S. K., & Leblanc, R. M. (2019). Carbon dots: Diverse preparation, application, and perspective in surface chemistry. *Langmuir*, 35(28), 9115–9132. https://doi.org/10.1021/acs.langmuir.9b00595