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Synthesis and Characterization of Carbon Dots Derived from *Citrullus lanatus* Rinds in Solid and Liquid States

Jacob Nkereuwem Jacob., Phebe Chukwunonye Okafor.[1], Maxwell Momah.[2], Osahon Kennedy Ogbeide[1] and Favour Ogheneyerowo Samuel[1]

[1]Analytical and Environmental Research Laboratory, Department of Chemistry, University of Benin, Edo State, Nigeria.
[2]Department of Chemical Sciences, University of Delta, Agbor, Delta State, Nigeria.

Corresponding Author: Jacob Nkereuwem Jacob: Email: jacob.jacob@uniben.edu

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ABSTRACT

Citrullus lanatus (watermelon) rinds, a major organic waste from fruit consumption, can serve as a sustainable precursor for carbon-based nanomaterials. This research presents the green synthesis and comparative characterization of carbon dots (CDs) derived from watermelon rinds in solid and liquid states. The rinds were dried, carbonized at 220 °C for two hours, and subjected to solvothermal synthesis. The synthesized CDs were characterized using Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), Dynamic Light Scattering (DLS), Ultraviolet-Visible (UV-Vis) Spectroscopy, and Scanning Electron Microscopy with Energy Dispersive X-ray (SEM-EDX). The solid-state and liquid-state CDs displayed average particle sizes of 3.62 nm and 19.4 nm, respectively, with polydispersity indices of 0.245 and 0.247, indicating moderate dispersion. UV-Vis analysis revealed absorption peaks at 286 nm (solid) and 280 nm (liquid), while FTIR spectra confirmed the presence of C=C, O–H and C–H functional groups. XRD confirmed amorphous graphitic structures, and SEM-EDX showed high carbon and nitrogen content. The findings suggest that watermelon rind-derived carbon dots possess tunable optical and structural properties suitable for bioimaging, sensing, and optoelectronic applications, promoting waste valorization and sustainable nanomaterial production.

Keywords: Carbon dots, Watermelon rinds, Green synthesis, Solid-state carbon dots, Liquid-state carbon dots, Biowaste valorization

INTRODUCTION

Nanotechnology has emerged as a pivotal field influencing diverse applications ranging from medicine and electronics to environmental remediation. Carbon dots (CDs), a subclass of carbon-based nanomaterials with sizes typically below 20 nm, have attracted increasing interest due to their superior optical, electrical, and biocompatible properties (Xu *et al.*, 2004; Wang *et al.*, 2017). Compared to conventional nanoparticles, CDs offer advantages such as cost-effectiveness, chemical stability, photoluminescence, and environmental friendliness (Eskalen *et al.,* 2021).

Traditional synthesis methods for CDs usually involve toxic precursors and energy-intensive processes, resulting in environmental concerns. Green synthesis provides an eco-friendly alternative by utilizing biological waste as raw materials (Osman *et al.,* 2024). Among various biowastes, fruit rinds have demonstrated high potential as carbon sources. *Citrullus lanatus* (watermelon) rinds, an abundant agricultural residue, presents a sustainable feedstock for CDs synthesis due to its carbon-rich composition (Gin *et al.,* 2014).

Fruits are taken on a regular basis in Nigeria due to their high vitamin, mineral, and fiber content. However, in most situations, just the edible pulp is used, with the seeds and skins discarded. This results in a substantial accumulation of agricultural trash, notably fruit rinds, which pose environmental concerns when not adequately managed. The disposal of these rinds has become a significant concern, with potential environmental effects. As a result,

there is an increasing demand for comprehensive research into the nutritional and industrial applications of fruit waste (Gin *et al.*, 2014).

Watermelon (*Citrullus lanatus*) ranks among fruits widely eaten globally, leading to substantial peel waste. Researchers have investigated methods to repurpose these rinds, transforming them into valuable materials. This method utilizes a low-temperature carbonization and filtration process, and successfully synthesized fluorescent CDs of high quality. The procedure involved heating the rinds at 220°C for two hours in an Oxygen-rich environment, followed by 15 minutes of sonication, filtration, and high-speed centrifugation as shown in Fig.

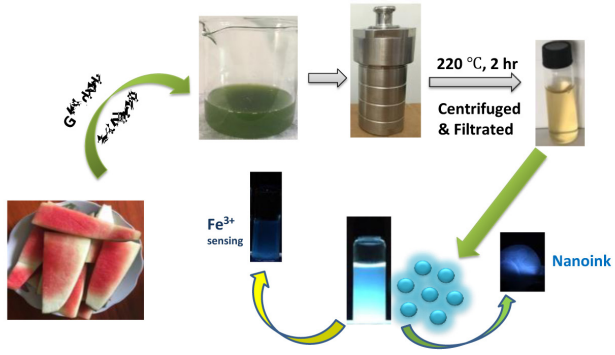


Figure 1: The Schematic Pathway of synthesized CDs from watermelon for purposeful applications (Kwee *et al.*, 2022)

This aim of this study was to synthesize and characterize carbon dots from watermelon rinds using a green approach and to compare their physicochemical and optical properties in solid and liquid states. Comparative evaluation of solid and liquid-state carbon dots is required to understand physicochemical and state-dependent optical properties, especially fluorescence behavior, aggregation effects, and application-specific performance (Borgohain *et al.*, 2021; Liu *et al.,* 2019; Fu *et al.,* 2024). This study contributes to the production of highly efficient carbon-dot-based materials and also advance sustainable nanomaterial production from agricultural waste.

MATERIALS AND METHODS

Materials

Citrullus lanatus rinds were obtained from Ugbowo Market, Edo State, Nigeria. The sample was identified and authenticated (Voucher No: UBH-C401) in the Department of Plant Biology and Biotechnology, University of Benin, Nigeria.

Synthesis of Carbon Dots

Liquid-State Carbon Dots (LCDs):

A freshly collected watermelon rinds were washed multiple times with distilled water to eliminate dirt and adhering sediments. After cleansing, the rinds were left to dry under sunlight for several days to reduce moisture content. Once dried, they were subjected to carbonization in a furnace at 220 °C for two hours in the presence of air. The carbonized rinds were then ground into a fine powder. A precisely measured 1 gram of this powder was dispersed in 100 mL of deionized water and sonicated for 15 minutes to achieve a uniform dispersion. The resulting solution was then filtered using a filter paper, followed by centrifugation at 10000 rpm for 15 minutes. The supernatant, which contained luminescent carbon dots, was subsequently analyzed using various analytical techniques (Sarada *et al.*, 2015; Zhou *et al.,* 2012)

Solid-State Carbon Dots (SCDs):

Ten gram of ground rinds was measured and added to1000 mL deionized water. The mixture was poured in a conical flask and sonicated for 30 minutes for homogeneous dispersion. The dispersed solution was centrifuged at 10000 rpm and the resultant residue was dried in the oven at 70 °C for 8 hours. The powdered solid containing the carbon dots were characterized by various techniques (Zhou *et al.*, 2012; Kukreja *et al.*, 2015 with modifications). This research was carried out once, after a successful preliminary study.

Characterization Techniques used:

- **FTIR**: Identified functional groups and bonding characteristics.
- **XRD**: Determined structural crystallinity.
- **DLS**: Measured hydrodynamic particle size and polydispersity.
- **UV-Vis**: Examined optical absorption and transitions.
- **SEM-EDX**: Assessed morphology and elemental composition.

RESULTS AND DISCUSSION

Dynamic Light Scattering (DLS)

The average hydrodynamic diameter of SCDs and LCDs was 95.35 and 40.97 nm respectively. Both had polydispersity indices below 0.30 (0.245 for SCDs and 0.247 for LCDs), suggesting uniform particle distribution (Figures 2 and 3). The smaller particle size of the SCDs indicates a more compact structure, while the LCDs' larger size reflects solvation and surface functionalization effects (Mancini *et al.,* 2023).

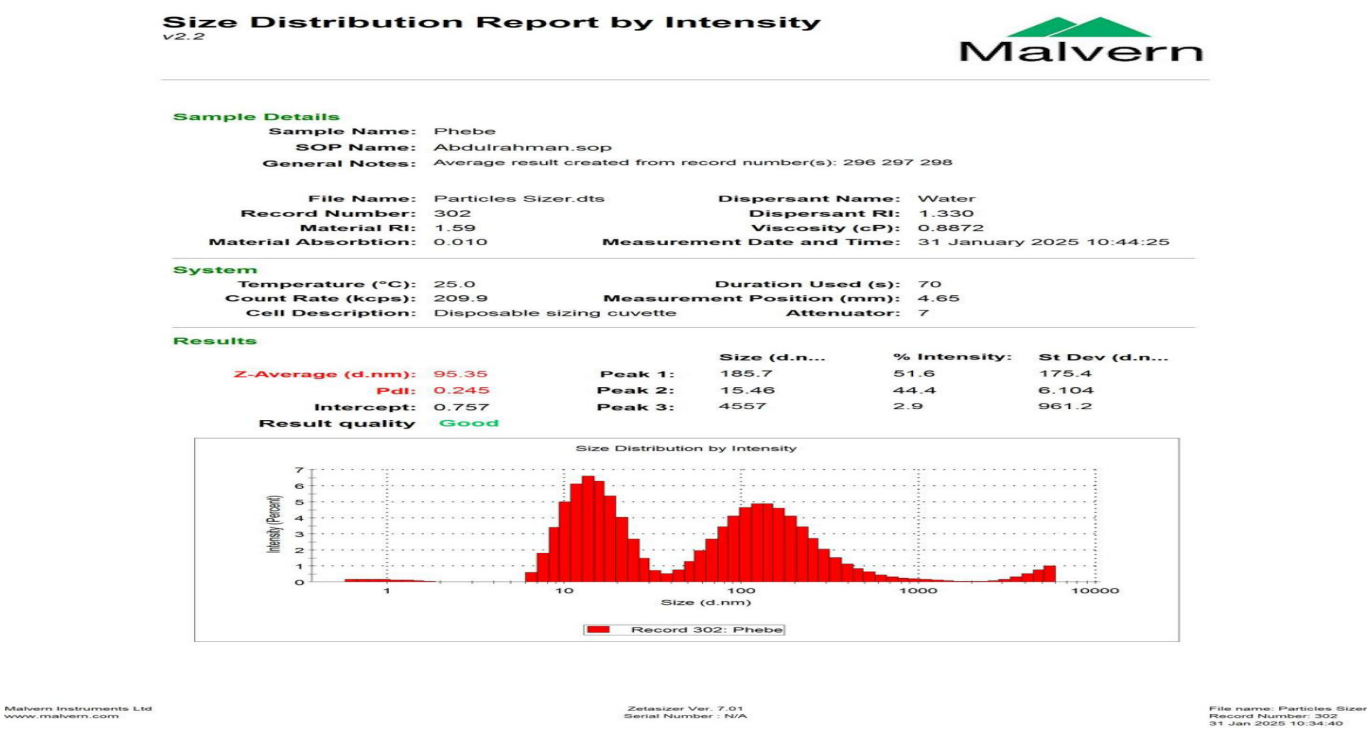


Figure 2: Size Distribution by Intensity for SCDs

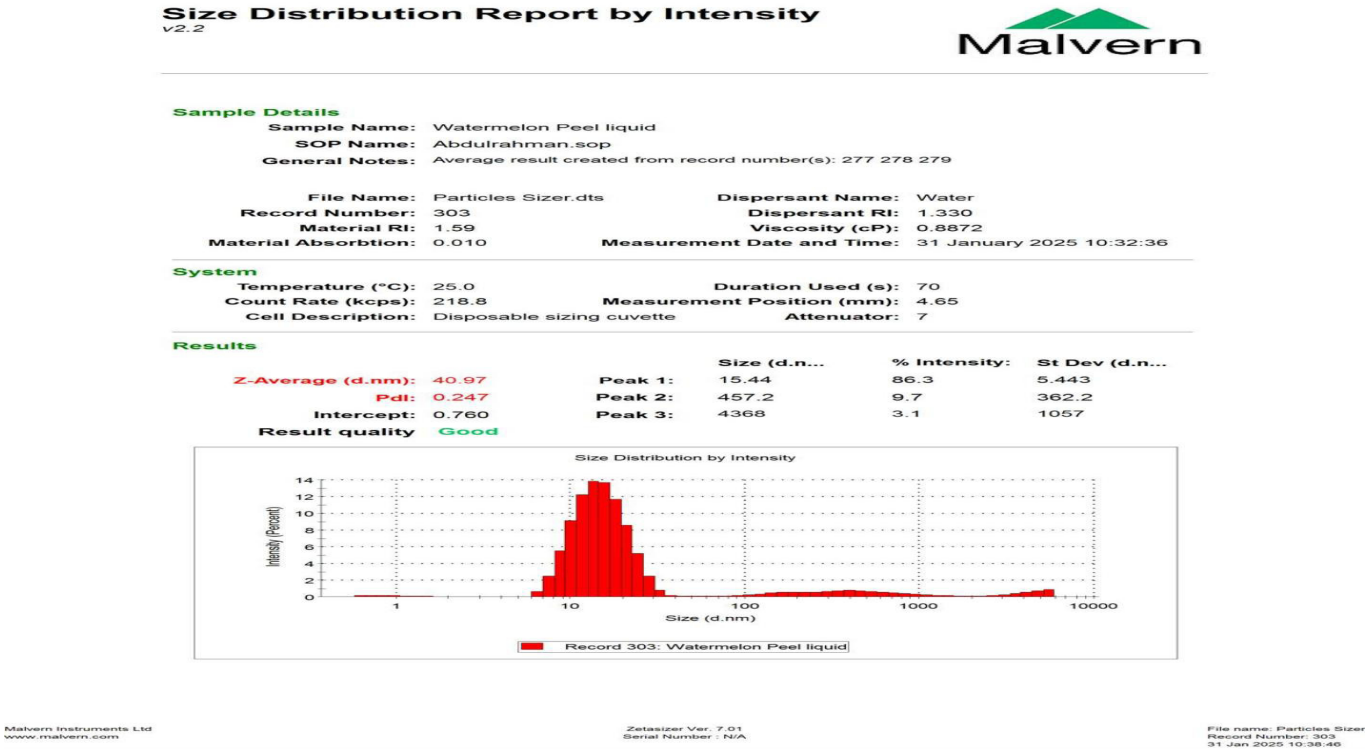
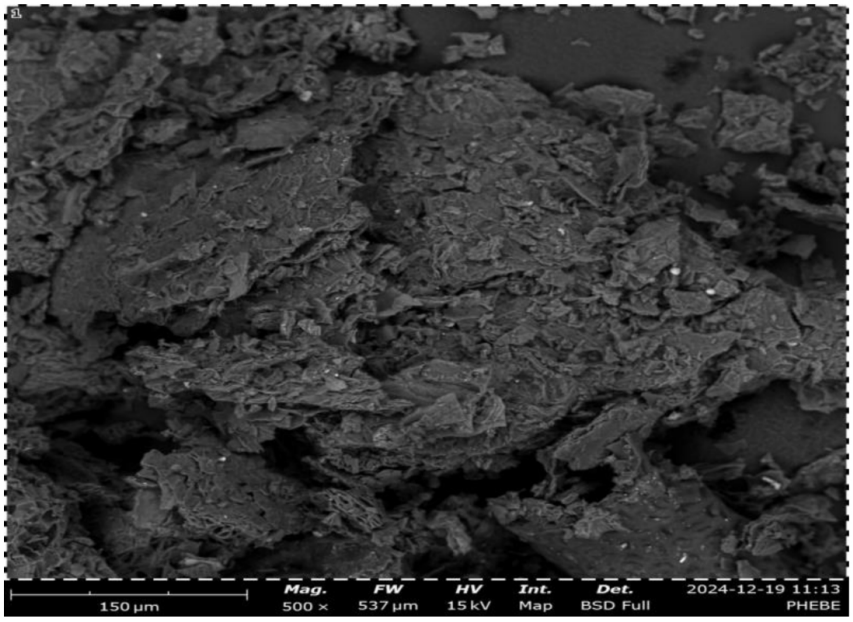


Figure 3 : Size Distribution Report by Intensity of LCDs

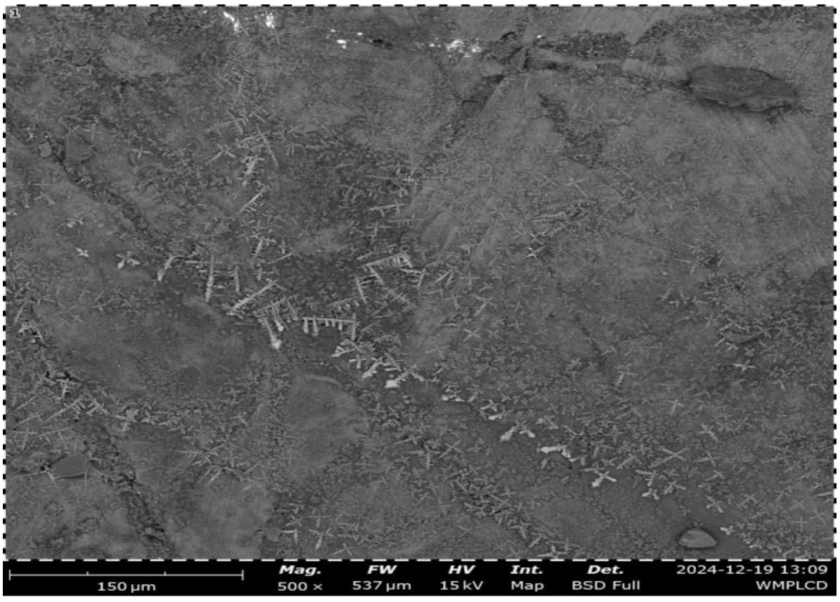
SEM-EDX Analysis

SEM images revealed that both solid and liquid states CDs were spherical with tendencies toward agglomeration. EDX confirmed that carbon and nitrogen were the predominant elements, accounting for 54.92% and 22.00% atomic concentration in SCDs, and 26.01% and 17.20% in LCDs (Figures 4 and 5). The heteroatom doping enhances fluorescence and solubility (Jing *et al.*, 2023).



Element Number	Element Symbol	Atomic Conc.	Weight Conc.
6	C	54.92	36.95
20	Ca	7.79	17.49
7	N	22.00	17.26
19	K	7.14	15.64
12	Mg	2.45	3.33
15	P	1.56	2.71
13	Al	1.76	2.66
14	Si	1.44	2.27
17	Cl	0.41	0.82
16	S	0.37	0.66
11	Na	0.15	0.20
22	Ti	0.00	0.00
25	Mn	0.00	0.00
26	Fe	0.00	0.00

Figure 4: SEM -EDX Result SCDs



Element Number	Element Symbol	Atomic Conc.	Weight Conc.
19	K	21.66	35.67
12	Mg	13.78	14.11
6	C	26.01	13.16
7	N	17.20	10.15
17	Cl	6.61	9.87
14	Si	5.10	6.03
11	Na	5.74	5.56
15	P	1.93	2.51
16	S	1.22	1.64
20	Ca	0.76	1.28
22	Ti	0.00	0.00
25	Mn	0.00	0.00
26	Fe	0.00	0.00

Figure 5: SEM -EDX Result for LCDs

UV-Visible Spectroscopy

The UV-Vis spectra displayed absorption peaks at 280 nm (LCDs) and 286 nm (SCDs), attributed to π–π^* transitions of aromatic C=C bonds (Figures 6 and 8). The blue fluorescence observed under UV illumination in Figure 7 for LCDs indicates successful formation of fluorescent carbon dots (Sun *et al.,* 2006).

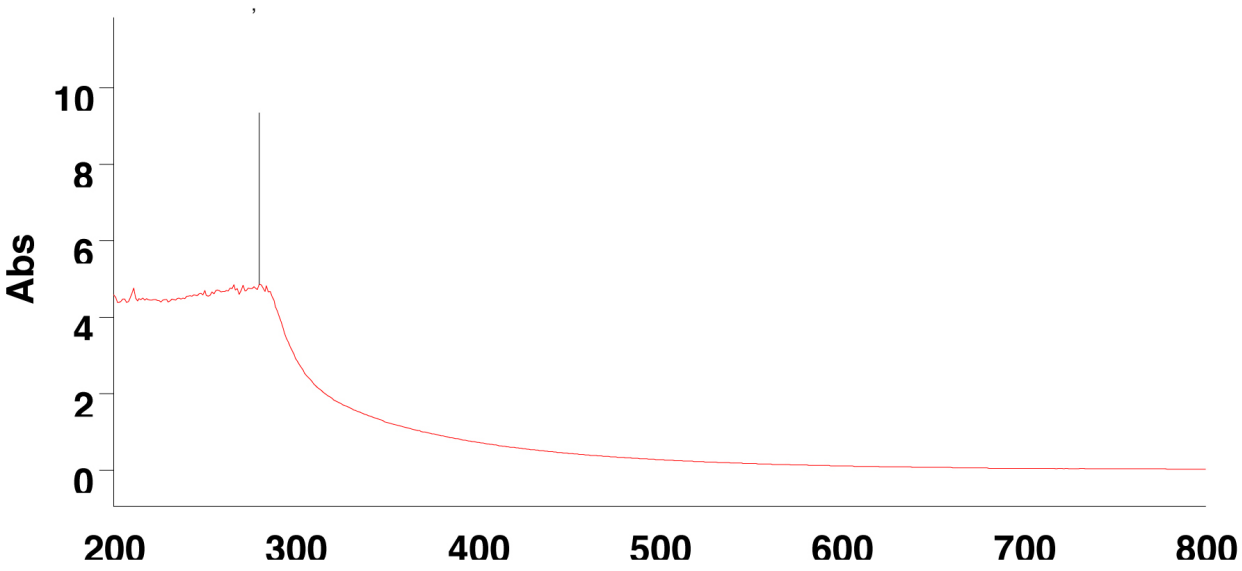


Fig. 6: UV-Vis Absorption Spectra for LCDs

(A) **(B)**

Figure 7: LCDs (A) in the absence of UV-light, (B) in the presence of UV-light.

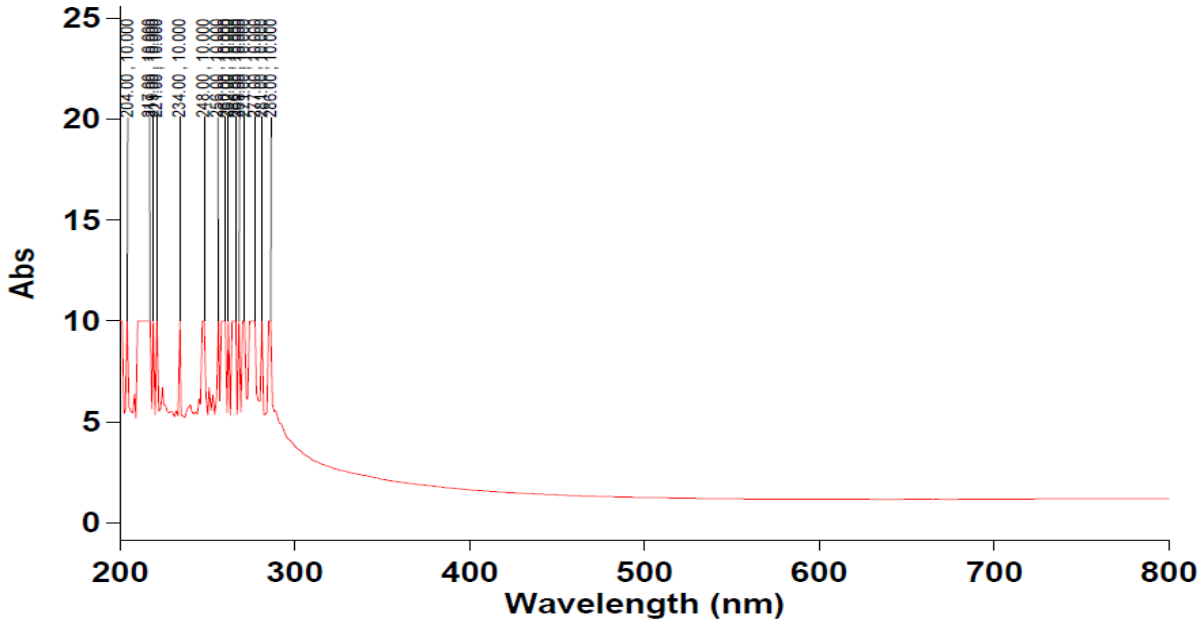


Figure 8: UV-VIS Absorption Spectra for SCDs

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra for LCDs and SCDs are shown in Figures 9 and 10. FTIR spectra of LCDs revealed peaks at 3336 cm^{-1} (O–H), 2081 cm^{-1} (C–H), and 1636 cm^{-1} (C=C), while SCDs showed bands at 3321 cm^{-1} (O–H), 2922 cm^{-1} (C–H), 1628 cm^{-1} (C=C), and 1155 cm^{-1} (C–O). These functional groups contribute to surface passivation and water solubility, enhancing optical properties (Roy *et al.*, 2015).

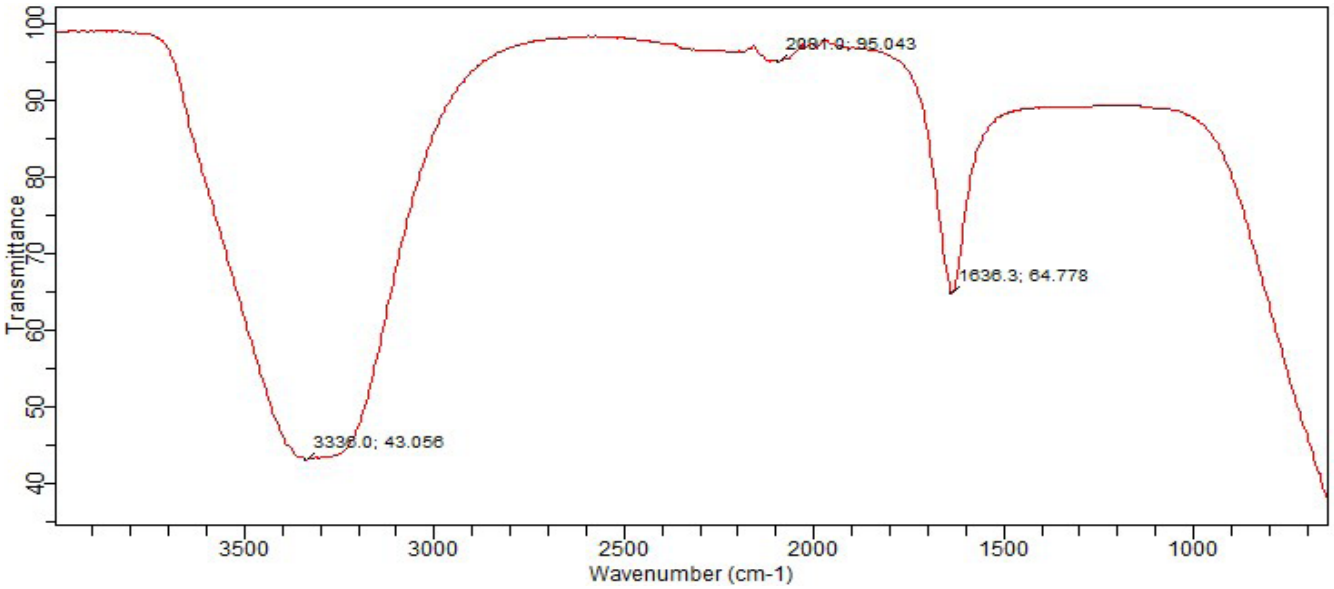


Figure 9: FT-IR Spectra of LCDs

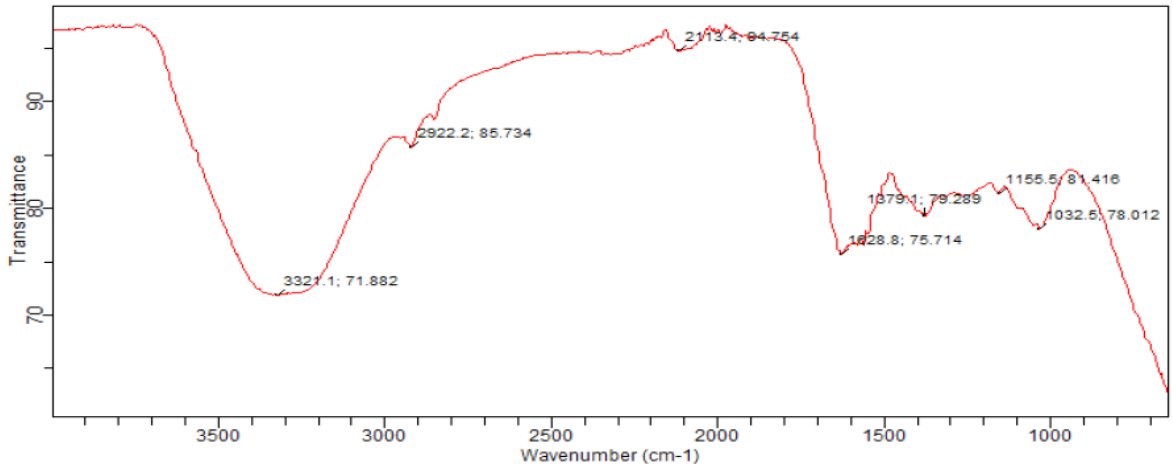


Figure 10: FT-IR Spectra for SCDs

3.5 X-Ray Diffraction (XRD)

XRD analysis results for LCDs and SCDs are shown in Figures 11 and 12 respectively. LCDs displayed a weaker peak near 15.5°, possibly due to the presence of graphene oxide layers (Dreyer *et al.,* 2010). The SCDs exhibited a broad diffraction peak at $2\theta \approx 20.3°$, typical of amorphous graphitic carbon. Using the Scherrer equation, the crystallite/domain sizes were estimated as 3.62 nm (solid) and 19.4 nm (liquid). Although the carbon dots show predominantly amorphous features, the presence of weak/broad diffraction features suggests limited short-range graphitic ordering. Therefore, the Scherrer equation was used to estimate the apparent size of coherent graphitic domains These results are in agreement with Liu *et al.* (2020) research findings.

General information

Analysis date	2024-12-20 13:57:15	Measurement start time	2024-12-19 15:47:51
Analyst	Default	Operator	Default
Sample name	WATER MELON PEEL LIQUID CARBON DOTS	Comment	
Measured data name	C:\WallPaper\19-12-2024\WATER MELON PEEL LIQUID CARB...	Memo	

Peak list

No.	2θ, °	d, Å	Height, cps	FWHM, °	Int. I., cps°	Int. W., °	Asymmetry	Decay(ηL/mL)	Decay(ηH/mH)	Size, Å
1	15.4(2)	5.73(8)	209(30)	4.3(3)	1563(91)	7.5(15)	0.59(14)	0.0(4)	1.55(13)	19.4(14)

No.	2θ, °	Phase Name	Chemical Formula	Card No	Norm. I.	Profile Type	Distributi...	Degree of Orientation
1	15.4(2)	Refikite: 1 2 1,Marialite: 2 0 0,...	C20 H32 O2,(Na3....	00-028-2009,01-07...	100.00	Split pseudo-Voigt	-	-

No.	2θ, °	Ring Factor	β Cluster
1	15.4(2)	-	-

Qualitative Analysis Results

Phase name	Formula	Figure of merit	Phase reg. detail	Space Group	DB Card Number
Refikite	C20 H32 O2	1.180	S/M(PDF-4 Minerals 2025)	18 : P21212	00-028-2009
Chaoite	C	2.861	Import(PDF-4 Minerals 2025)	147 : P-3	00-022-1069
Marialite	(Na3.35 Ca0.38 K0.24) (Si8....	2.740	Import(PDF-4 Minerals 2025)	87 : I4/m	01-070-6155
Mascagnite	(N H4)2 S O4	2.756	Import(PDF-4 Minerals 2025)	62 : Pmcn	00-001-0363
Aluminum Phosphate	Al P O4	1.608	Import(PDF-4 Minerals 2025)		00-015-0264

Figure 11: XRD Result for Synthesized LCDs

SWPCD_20241219_153850_G02_S02_M02-Evaluation report (SWPCD's_20241219_153850_G02_S02_M02)

General information

Analysis date	2024-12-20 13:48:52	Measurement start time	2024-12-19 15:44:05
Analyst	Default	Operator	Default
Sample name	SOLID WATERMELON PEELS CARBON DOTS	Comment	
Measured data name	C:\WallPaper\19-12-2024\PHEBE_20241219_153850_G02_S02...	Memo	

Peak list

No.	2θ, °	d, Å	Height, cps	FWHM, °	Int. I., cps°	Int. W., °	Asymmetry	Decay(ηL/mL)	Decay(ηH/mH)	Size, Å
1	20.31(11)	4.37(2)	585(68)	23.3(7)	27172(882)	46(7)	0.56(4)	1.47(3)	1.44(3)	3.62(10)

No.	2θ, °	Phase Name	Chemical Formula	Card No	Norm. I.	Profile Type	Distributi...	Degree of Orientation
1	20.31(11)	Graphite: 0 0 2,Quartz: 1 0 0,M...	C,Si O2,(Na3.21 Ca...	00-001-0640,00-00...	100.00	Split pseudo-Voigt	-	-

No.	2θ, °	Ring Factor	β Cluster
1	20.31(11)	-	-

Qualitative Analysis Results

Phase name	Formula	Figure of merit	Phase reg. detail	Space Group	DB Card Number
Graphite	C	0.756	Import(PDF-4 Minerals 2025)	147 : P-3	00-001-0640
Quartz	Si O2	1.451	Import(PDF-4 Minerals 2025)	154 : P3221	00-001-0649
Marialite	(Na3.21 Ca0.68 K0.11) (Si8....	1.442	Import(PDF-4 Minerals 2025)	87 : I4/m	01-070-6156
Goethite	Fe2 O3 · H2 O	3.012	Import(PDF-4 Minerals 2025)		00-001-0401

Figure 12: XRD Result for Synthesized SCDs

Comparative Analysis

Property	Solid-State CDs	Liquid-State CDs
Average Size	3.62 nm	19.4 nm
Absorption Peak	286 nm	280 nm
Major Functional Groups	C=C, O–H, C–H, C–O	C=C, O–H, C–H
Dominant Elements	C, N	C, N, K
Fluorescence	Limited	Strong blue
Suggested Applications	Optoelectronics, Sensors	Bioimaging, Drug Delivery

CONCLUSION

This study successfully synthesized and characterized solid and liquid states carbon dots from watermelon rinds through a green, low-temperature carbonization process. The solid-state CDs exhibited smaller particle size and higher carbon content, while liquid-state CDs showed enhanced fluorescence and solubility. The study demonstrates that watermelon rind waste can be effectively valorized into functional carbon nanomaterials suitable for use in bioimaging, optoelectronics, and environmental applications.

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