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Novel one-step synthesis of solid-state carbon dots by heating at around melting point of polyethylene terephthalate (PET) bottle plastic waste

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Abstract

Production of luminescent carbon dots (CDs) in the solid state has been a crucial challenge due to their tendency to self-aggregate, leading to fluorescence quenching and limiting their applicability in the solid state. In this work, we present an environmentally friendly method for producing solid-state CDs with high photoluminescence (PL) intensity by simple one-step heating method using waste PET bottle plastic as the raw material. Based on the PET thermal decomposition, heating temperatures between 200 °C and 300 °C and heating duration were explored. Through systematic experimentation, we discovered that heating temperature and time play a crucial role in controlling

PL intensity, ultraviolet-visible (UV-Vis) absorption, carbonization degree, and structure of CDs. The carbonization of CDs occurs when the heating temperature exceeds the PET melting point, resulting in strong PL characteristics in the range of 400 and 600 nm. However, when the temperature rises, the PL decreases as the number of oxygen-containing functional groups on the surface of CDs increases. The optimal conditions for high PL intensity were 260 °C for 2.5 hours. Our one-step heating approach provides a cost-effective solution for recycling PET waste, offering promising potential for various applications.

Keywords: carbon dots, solid-state fluorescence, polyethylene terephthalate, melting point

1. Introduction

Plastic bottles are commonly encountered packaging materials due to their versatility, durability, and low cost (Benyathiar et al., 2022; Rodríguez-Hernández et al., 2019). It is expected that around 62% of all plastic bottles have been made from polyethylene terephthalate (PET) (Amirudin et al., 2022; Becerril-Arreola and Bucklin, 2021; Zhang et al., 2020). Nowadays, it is very convenient to use PET bottles as single-use beverage packaging. Consequently, disposable PET bottles accumulate as waste and become a significant environmental concern due to their non-biodegradable properties. The biodegradation of PET waste can take up to 500 years and releases harmful toxins into the water and soil, posing risks to human health and biodiversity (Becerril-Arreola and Bucklin, 2021; Gao et al., 2022; Ghosh and Das, 2021). Incineration is a common method for disposing of PET waste, but it contributes to air pollution and releases high CO_2 emissions that exacerbate greenhouse effects and climate change (Song et al., 2019; Yin et al., 2021). Thus, there is a pressing need for a more environmentally friendly method to increase the value of these waste materials. Recently, alternative methods have been developed to process PET wastes as a promising source for synthesis of carbon-based nanomaterial, such as carbon dots (CDs) (Ghosh and Das, 2021; Hu et al., 2021, 2019; Johnson et al., 2021; Rodríguez-Hernández et al., 2019).

CDs are a promising class of zero-dimensional carbon-based nanomaterial that have gained significant attention for their outstanding properties, such as chemical stability, low toxicity, and good optical stability, showing promising potential for many advanced applications (Bagheri et al., 2017; Song et al., 2019). Their characteristics and states can be tunable depending on their application (Mansuriya and Altintas, 2021). In recent years, there has been an increased demand for solid-state CDs in optoelectronic devices, sensors, fingerprint identification, fluorescent ink, security label, and others (Jin et al., 2020; Singaravelu et al., 2021; Wang et al., 2020). However, solid-state CDs always suffer from fluorescent quenching due to direct π-π interactions or excessive fluorescence resonance energy transfer (Ren et al., 2021; Singaravelu et al., 2021; Wang et al., 2020), which seriously limits their application in solid-state emissions. Currently, to obtain solid-state fluorescent CDs, many efforts have been made usually using two main strategies: (i) the synthesis of fluorescent self-quenching-resistant solid-state CDs, and (ii) blending CDs with polymers materials to restrict intermolecular motions (Ren et al., 2021; Singaravelu et al., 2021). The second strategy, however, involves a complicated fabrication process and can reduce the optical performance of CDs (Yoo et al., 2019). Therefore, there is need for the development of solid-state CDs that are substantially resistant to self-quenching.

Plastic-based CDs are a great candidate among the various solid-state CDs since they naturally have hydrophobic qualities, as highlighted by Yin et al (Song et al., 2019). PET plastic-based CDs, in particular, may also show potential, given their similar properties. Although the final product is liquid-state CDs, several studies of PET-based CDs have been performed using a two-step synthesis method. Ghosh and Das reported the heating of PET to high temperatures at the first step of synthesis, producing a dark and dry powder resembling carbon black (Ghosh and Das, 2021). Similarly, Hu et al. also conducted a two-step synthesis with the heating of PET at the first step (Hu et al., 2021). However, if the carbonization temperature is optimized, solid-state CDs with high fluorescent can be yielded without requiring a second synthesis step. As Bagheri and his coworkers reported, the optimum carbonization degree in the synthesis CDs was affected by melting point of starting material during heating process. The photoluminescent behavior of CDs strongly depends on the temperature of heating during synthesis (Bagheri et al., 2017). To the best of our knowledge, there have been no reports on the investigation of PET-based CDs in a solid state. Specifically, synthesis according to the thermal decomposition of PET has not been considered.

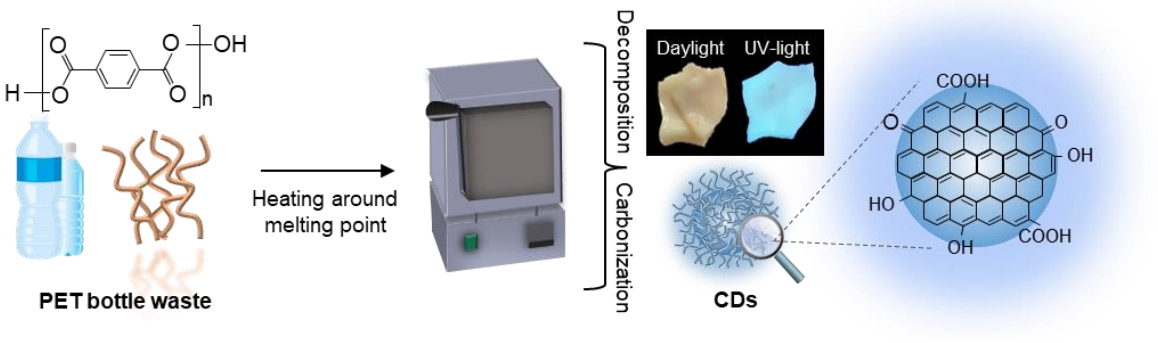
This study reported a simple synthesis route for producing solid-state CDs from PET plastic waste. An experiment plan was arranged to gather the maximum information possible regarding the formation of these materials and the impact of synthesis conditions on their optical and chemical composition. The heating temperatures were investigated around the melting point of PET because carbon chains in the polymer decompose at temperatures above the melting point, which may lead to nucleation processes generating carbon cores. This study opens up a new understanding of the melting temperature as a critical point for synthesizing CDs which only a few researchers have pointed out. In addition, the synthesis process does not require toxic, corrosive, or expensive solvents which are typically employed in synthesizing CDs. The production of solid-state fluorescent CDs from PET plastic waste increases the added value of PET waste and opens opportunities for future research in plastic waste management.

2. Material and Methods

Synthesis of CDs. The solid-state CDs were prepared by a one-step heating method using PET bottle waste as a carbon source. First, a waste PET bottle was collected and washed subsequently using water. The dried PET bottle was cut into small flakes and, afterward, transferred in a crucible for air oxidation in a muffle furnace at various temperatures ranging from 200 °C to 300 °C for 2.5 hours. The optimal temperature was determined to be 240°C and was selected for the heating durations of 1 hour to 3 hours. The resulting solid-state product was collected and then characterized.

Characterization. UV-visible absorption spectra were recorded using a BMG Labtech Fluostar Omega spectrometer. Fluorescence measurements were carried out using a Cary Eclipse MY14440002 spectrofluorometer. Integrated fluorescence intensity is the area under the PL curve in the wavelength range from 400 to 650 nm. Fourier Transform Infrared (FTIR) spectra were recorded for powder CDs using the Perkin-Elmer Spectrum Version 10.03.06 with an ATR attachment. Thermogravimetric analysis (TGA) was performed using a Hitachi STA200RV with a heating rate of 20 °C/min. Raman spectroscopy was measured using Horiba LabRAM HR Evolution Laser 785 nm.

3. Results and Discussion



Scheme 1. Mechanism for the preparation of solid-state CDs based on PET bottle waste

The solid-state CDs were synthesized from PET bottle waste using a simple heating process in a muffle furnace without any additional chemicals (Scheme 1). In preparing CDs using the heating method, the PET chains were decomposed, followed by carbonization and then solid-state CDs were formed. In this study, a systematic synthesis study was conducted by setting the synthesis temperature at around the melting point of PET and varying the heating duration to get the maximum information possible. The DTA of PET bottle waste (Fig. 1a) showed a strong endothermic peak at around 250 ^{o}C, implying a change in PET composition at this temperature. On the other hand, the TGA curve (Fig 1b and c) confirmed a decrease in molecular weight, with the thermal degradation of PET onsets at lower temperatures (30^{o}C). Furthermore, FTIR analysis shows that PET plastic bottles (Fig. 2d) showed the presence of broad molecular groups consisting of carbon, hydrogen, and oxygen. The C-H stretching vibration modes appear in the region 3000-2825 cm^{-1} that refer to the functional groups such as alkyl, alkanal, alkyne, alkene, and arene. The C-H bending mode of vibration, which has weaker bond strength than their stretching modes, appears in the region 924-808 cm^{-1} and 573 cm^{-1} (Prasad et al., 2011). The absorption at 3412 cm^{-1} is assigned to the O-H stretching at the end group of the PET molecule chain. The C=O stretching and the aromatic skeleton stretching bands were observed at 1730 and 1614 cm^{-1}, respectively (Torres-Huerta et al., 2016).

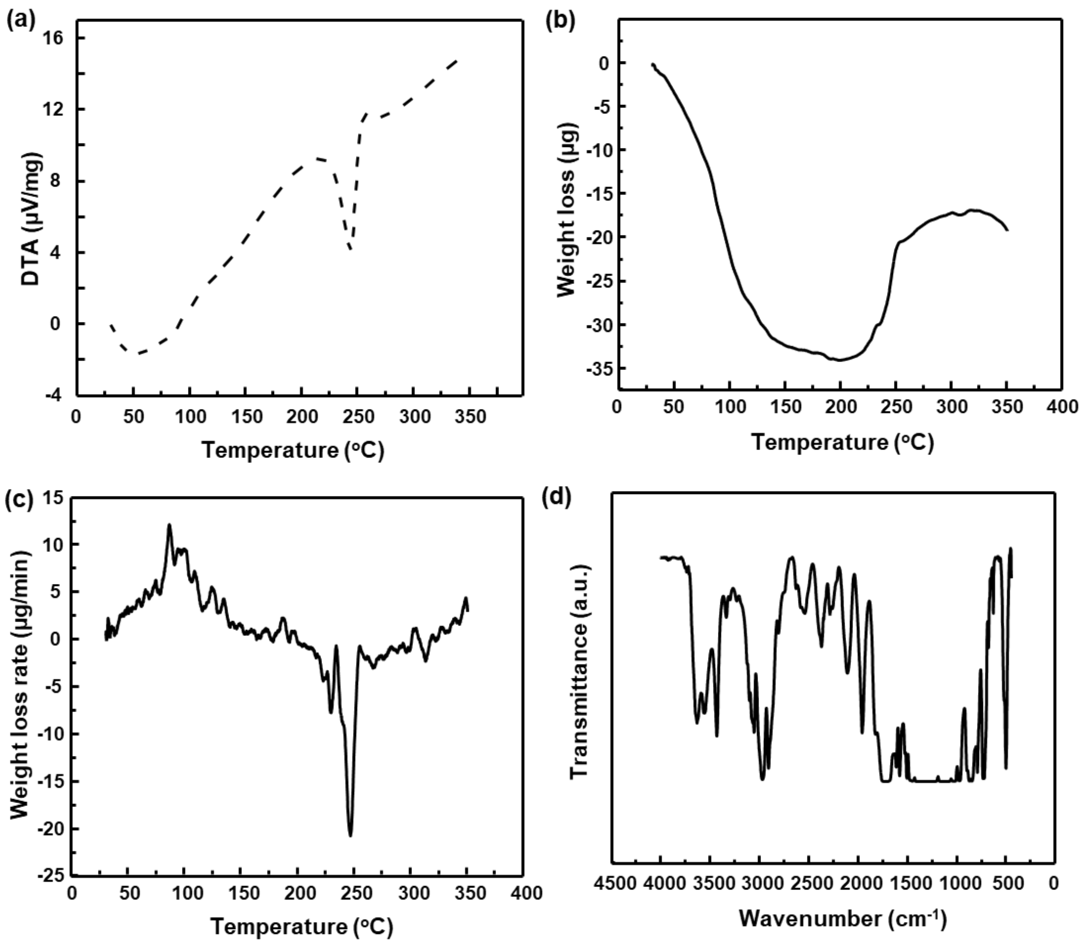


Figure 1. Starting material (PET bottle waste) analysis: (a) differential thermal analysis, (b) thermogravimetric analysis (TGA), (c) derivative TGA (DTGA), and (d) Fourier Transform Infrared Spectroscopy (FTIR).

The distribution of the samples with different heating temperatures is shown in Fig 2a. Physically, the samples heated at temperatures ranging from 200 to 240 °C (below the melting point) remained transparent but exhibited increased brittleness and shrinkage compared to the unheated sample. On the other hand, the samples heated over the melting point (260-300°C) showed significant physical alteration, such as becoming opaque, extremely brittle, and undergoing a color from light brown to dark brown. Moreover, under UV light, the results revealed that samples heated between 200-240^{o}C exhibited no luminescence. Meanwhile, samples of 260-300^{o}C showed luminescence, with samples of 260^{o}C having the brightest luminescence. This result indicated that determining the synthesis temperature around the melting point is one of the most crucial variables in producing CDs with excellent luminescence.

The UV-Vis absorption spectra of the samples with varying synthesis temperatures are depicted in Fig 2b. Samples at 200-240^{o}C were not characterized due to their high stickiness and very weak luminescence. The UV-Vis spectra displayed absorption in the UV region of 220-300 nm. A stronger peak was observed at 240 nm with a shoulder at 280 nm originating from π-π^* transition of C-C and C=C in aromatic rings of the carbon core and n-π^* transition of oxygen-related bonds (C=O and C-O) on the surface state of CDs, respectively (Ding et al., 2016; Y. Y. Liu et al., 2021). In the case of the 260°C sample (CDs-260), the peak at 240 nm was higher than in the other CDs, indicating that it has stronger absorption properties. This result supports the conclusion that the synthesis temperature has a significant effect on the absorption properties of the synthesized CDs (Zhang et al., 2016).

The PL spectra of the as-synthesized CDs at different temperatures are depicted in Fig 2c. Upon excitation at 360 nm, PL intensity also shows a similar trend as the 240 nm peak of CDs absorption intensity, suggesting the luminescence of solid-state PET-based CDs may originate from the π-π* bond transition in the carbon core. Widely proposed luminescence mechanisms of CDs originate from the conjugated π-domain within the graphitic carbon core, the surface state, or the molecular state of CDs (Ai et al., 2021; Xia et al., 2019). Here, the emission of PET-based CDs belonged to the core-state luminescence mechanism category. Under 360 nm irradiation, the luminescence of solid-state CDs centered at 450 nm, indicating blue color (in line with the physical appearance Fig.

2a). As shown in Figure 3d, the integrated fluorescence intensity is derived from the area under the PL curve in the 400 to 650 nm range. The PL intensity changes with heating temperature, and CDs-260 has the highest intensity. However, the PET-based CDs emit less light and look black when the heating temperature is quite higher than the melting point, indicating that carbonization occurs during the formation of CDs. Due to the severe aggregation-caused quenching, most CDs show no fluorescence in the solid state (B. Liu et al., 2021). This study obtained solid-state PET-CDs with strong blue photoluminescence without aggregation.

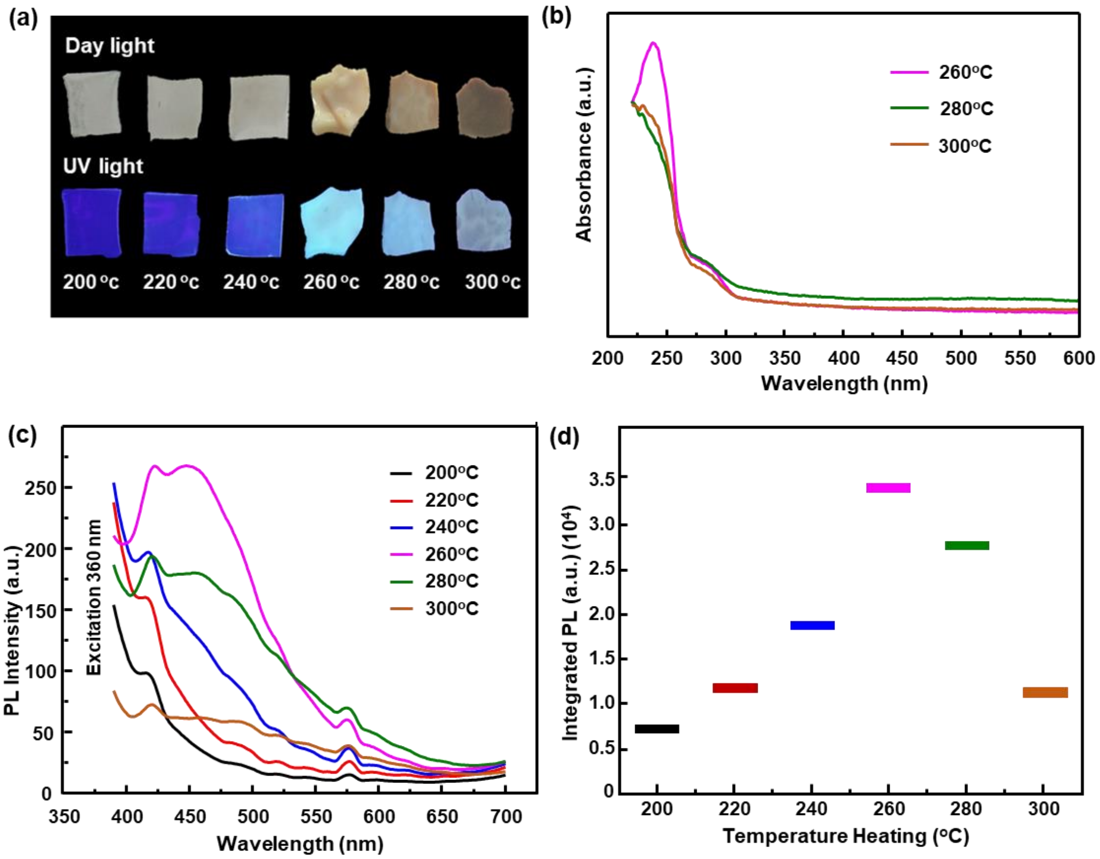


Figure 2. (a) Solid-state PET-based CDs under visible light (up) and UV radiation (down) over heating temperature variation, (b) UV-Vis absorption of solid-state PET-based CDs, (c) PL spectra

of the solid-state PET-based CDs samples under 360 nm, (d) integrated PL of spectra PL from 400 to 650 nm wavelength.

As shown in Fig. 3, Fourier Transform Infrared (FTIR) was performed to determine the composition of the PET-CDs. The FTIR results confirmed the presence of different functional groups in the synthesized CDs, including oxygen, hydrogen, and carbon (Fig. 3a). Compared to the FTIR results of untreated PET, some of the PET composition significantly changed after heating above the melting point, indicating decomposition occurred during the heating process (Fig 3a). The absorbance at 1430 cm^{-1} changed significantly, indicating a C-O group presence. The higher the temperature, the more energy the sample will attach to ambient oxygen. In addition, changes at 1670 cm^{-1} were observed, indicating conjugated C=C and C=O bonds (Fig. 3b). The untreated PET showed a C=C bond from the aromatic skeleton at 1610 cm^{-1} and the C=O bond from the carbonyl at 1720 cm^{-1}. However, when the PET was heated above the melting point, the C=C and C=O frequencies shifted and were no longer distinguishable, moving to 1660 cm^{-1} and indicating conjugation of the carbonyl group with a C=C double bond. The presence of the C=C and C=O bond signatures suggests forming a π-conjugated system as CDs core structure (Permatasari et al., 2021). This conjugation bond plays a role in the CDs photoluminescence process, which is related to the energy gap (Permatasari et al., 2021; Semeniuk et al., 2019; Wang et al., 2017). The results of this study demonstrate that temperatures above the melting point can lead to the formation of conjugate bonds in the aromatic skeleton of the PET-based CDs, resulting in solid luminescence. However, CDs-280 and CDs-300 have lower luminescence intensity (as previously demonstrated in Fig 2c) due to a large number of attached oxygen bonds. These oxygen-containing groups lead to non-radiative coupling of electron-hole pairs that suppress CDs PL (Ai et al., 2021). In addition, as depicted in Fig. 3c, PET-CDs feature C-H sp^3 bond vibrations between

3000 to 2800 cm^{-1}, suggesting the carbon core of the PET-CDs. In contrast, untreated PET possessed C-H sp^2 bonds that vanished upon heating, indicating that heating at temperatures above the melting point decomposed the original PET structure.

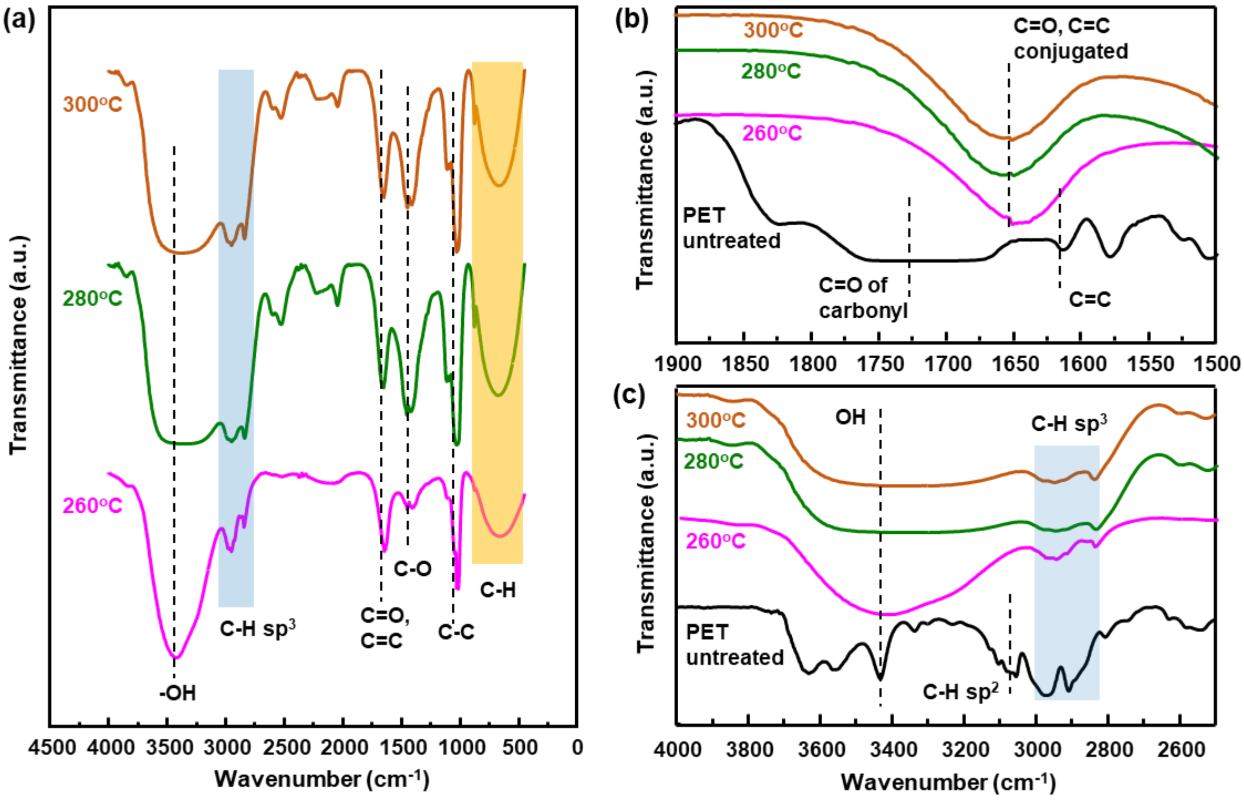


Figure 3. (a) FTIR spectra of PET-CDs with different temperature heating at full region, (b) FTIR spectra at C=C and C=O region of PET-CDs with different temperature heating compared with untreated PET, and (c) FTIR spectra at OH, C-H sp^2 and C-H sp^3 region of PET-CDs with different temperature heating compared with untreated PET.

The structural characteristics of the PET-CDs were further analyzed using Raman scattering, as shown in Fig 5. The PET-based CDs at 260°C exhibit a Raman peak at 1300 cm^{-1}, corresponding to the vibration of aromatic in-plane CH deformation (Xu et al., 2020). There were also peaks at 1620 and 1760 cm^{-1}, attributed to the ring C-C stretching and C=O stretching, respectively

(Aoyama et al., 2014). A peak at ~1300 cm^{-1} is often referred to as a peak from the out-of-plane vibrations of sp^2 carbon atoms in the presence of disordered states corresponding to topological sp^3 molecular defect states, while the peak at ~1620 cm^{-1} results from the in-plane stretching vibrations of sp^2 carbon atoms within aromatic domain (Bhattacharyya et al., 2017). However, at higher temperatures (300 ^{o}C), the spectral peak broadened, indicating that the structure of CDs became amorphous. This result implies, based on the emission spectra, that the structure of the CDs also affects the intensity of the generated emissions. Crystalline structures are expected to emit more optimally than amorphous structures due to reduced phonon (non-radiative) scattering losses (Pal et al., 2018).

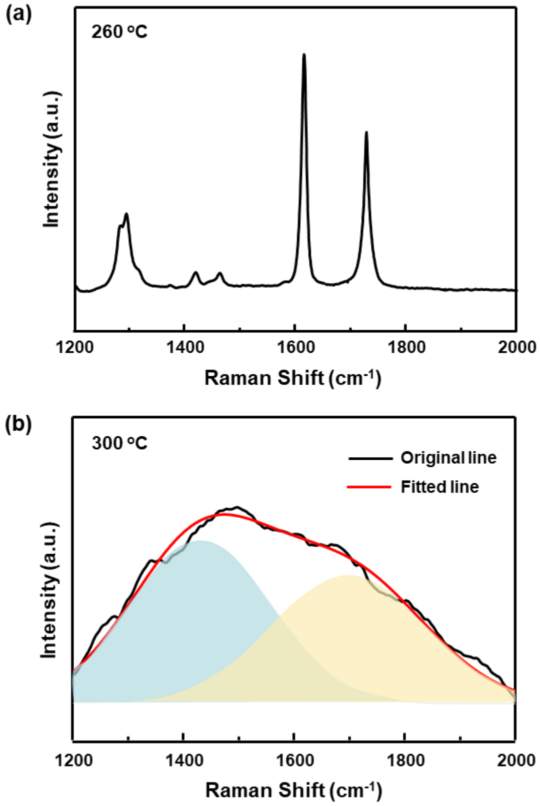


Figure 4. Raman shifts of PET-CDs by heating at: (a) 260 ^{o}C and (b) 300 ^{o}C

The role of reaction time on the properties of the materials is displayed in Fig 5. Again, the emission of the PET-based CDs strongly depends on the reaction time as well. The physical appearance of PET-based CDs (Fig. 5a) indicates that the sample is photoluminescent after being heated for more than 1 hour at a heating temperature over the melting point (260 ^{o}C). Optimal emission is observed in PET-based CDs heated for 2.5 hours, as demonstrated by the photoluminescence spectra shown in Fig. 5b. Modifying the heating time results in a shift in the emission peak of the PET-based CDs to 450 nm, similar to the variation observed with heating temperature. As illustrated in Fig 5c, the highest intensity of the PET-based CDs was observed at 2.5 hours of heating, followed by a decrease in intensity after heating for 3 hours.

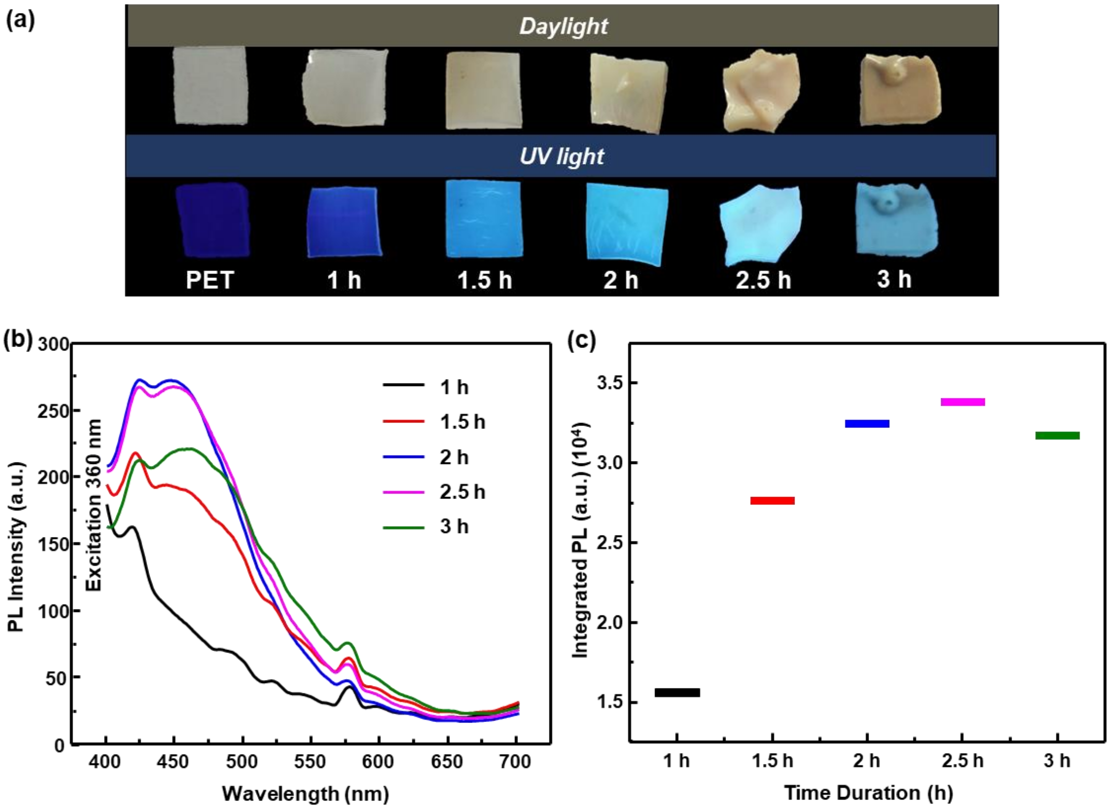


Figure 5. Dependence of the photoluminescence (PL) properties of CDs on heating time: a) physical appearance emission of PET-CDs, (b) PL spectra of PET-CDs, and (c) integrated PL as a function of time duration of hearing and PL intensity.

Fig 6 summarizes our findings. The schematic correlates the PL intensity of the PET-CDs obtained during different stages of heating, which is primarily attributed to the conjugation of the aromatic core. As the temperature increases, the number of oxygen-containing groups grows and contributes to the suppressed emission of the aromatic core. The optimal PL intensity is observed in PET-based CDs at 260 °C with a 2.5 h heating duration. Initially, the polymer of PET is non-fluorescent molecules. However, under low heating temperatures (below its melting point), the PET bonds do not decompose but become more wrinkled. When the degree of heating is increased above the melting point (260 °C), the PET carbon chain linkages decompose and carbonize, forming carbon core CDs with a conjugated aromatic core structure. This conjugation determines the photoluminescence properties of the CDs. At higher temperatures (from 280°C to 300°C), the carbon core gradually grows, and the number of oxygen-containing groups on the surface of PET-based CDs increases, leading to a decrease in the intensity of CDs. The duration of heating also has a significant impact on the intensity of PET-based CDs obtained. The carbon chain bonds decompose by heating PET above its melting point (260 °C), but sufficient heating time is necessary to generate an appropriate carbon core with conjugated bonds. In this study, the optimal duration was 2.5 hours. In conclusion, the PL intensity of PET-based CDs is influenced by the number of oxygen-containing groups and the growth of the carbon core so that the PET-based CDs with the highest intensity PL is obtained at appropriate heating temperature and duration.

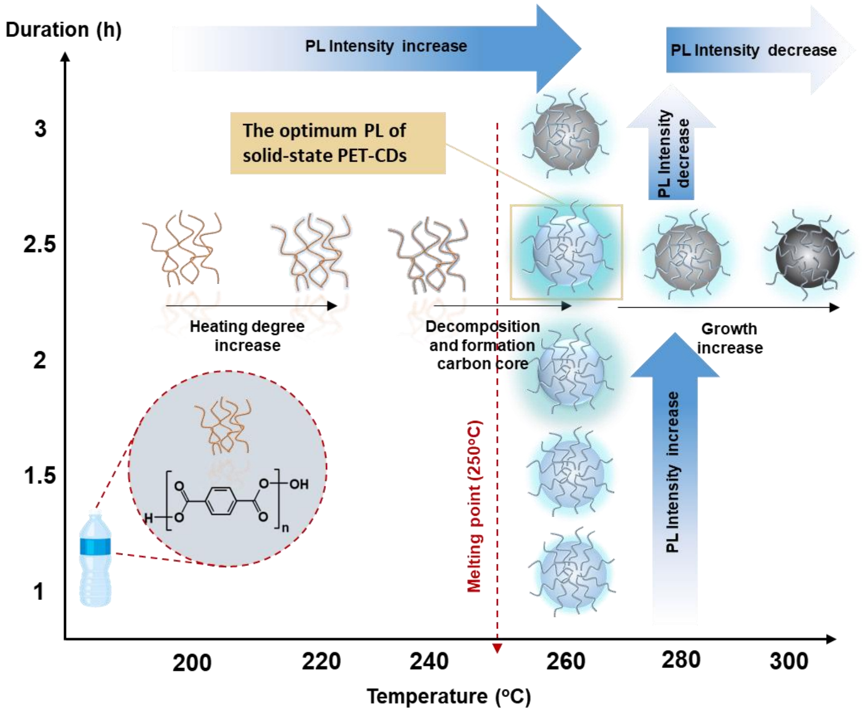


Fig 6. Schematic representation of the emission characteristics of PET-CDs over temperature and time scales and schematic possibility of mechanism of CDs formation.

4. Conclusions

In summary, we have demonstrated a one-step synthetic route to convert PET bottle waste into solid-state fluorescent CDs. The PL properties of the solid-state PET-CDs prepared by a heating method strongly depend on the temperature and duration. This study used the thermal decomposition (melting point) of PET to determine the synthesis temperature and could study the effect of that temperature on the PL properties of PET-based CDs. We discovered that PET-based CDs fabricated at 260 °C for 2.5 hours exhibit the highest fluorescence intensity. The results indicate that the melting point of PET plays a crucial role the in formation of conjugation aromatic core of CDs. The carbonization degree would increase not only at longer heating durations, but also as a result of higher heating temperatures after melting point. These findings offer a promising solution for plastic waste management and a simple, green synthesis route for the production of solid-state fluorescent CDs without the problem of self-quenching.

5. Author Contributions

Mahardika Prasetya Aji: original idea, conceptualization, supervision, and writing-review & editing. Ita Rahmawati: conceptualization, methodology, investigation, writing-original draft, and writing-review & editing. Aan Priyanto: writing-review & editing and visualization. Putut Marwoto: supervision and visualization.

6. Conflict of interest

There are no conflicts to declare.

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2. Bukti konfirmasi keputusan dan hasil review manuskrip

(11 Agustus 2023)

Mahardika Prasetya Aji <mahardika@mail.unnes.ac.id>

Decision on submission to Environmental Nanotechnology, Monitoring & Management

Environmental Nanotechnology, Monitoring & Management <em@editorialmanager.com>
Fri, Aug 11, 2023 at 1:32 AM
Reply-To: "Environmental Nanotechnology, Monitoring & Management" <support@elsevier.com>
To: Mahardika Prasetya Aji <mahardika@mail.unnes.ac.id>

CC: yolanda.pico@uv.es

Manuscript Number: ENMM-D-23-00365

Novel one-step synthesis of solid-state carbon dots by heating at around melting point of polyethylene terephthalate (PET) bottle plastic waste

Dear Mr Prasetya Aji,

Thank you for submitting your manuscript to Environmental Nanotechnology, Monitoring & Management.

I have completed my evaluation of your manuscript. The reviewers recommend reconsideration of your manuscript following major revision. I invite you to resubmit your manuscript after addressing the comments below. Please resubmit your revised manuscript by Aug 31, 2023.

When revising your manuscript, please consider all issues mentioned in the reviewers' comments carefully: please outline every change made in response to their comments and provide suitable rebuttals for any comments not addressed. Please note that your revised submission may need to be re-reviewed.

To submit your revised manuscript, please log in as an author at https://www.editorialmanager.com/enmm/, and navigate to the "Submissions Needing Revision" folder.

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Environmental Nanotechnology, Monitoring & Management values your contribution and I look forward to receiving your revised manuscript.

Kind regards,
Piero Gardinali
Co Editor-in-Chief

Environmental Nanotechnology, Monitoring & Management

Editor and Reviewer comments:

Reviewer #1: In this manuscript, some experiments were conducted to obtain the so-called CDs from PET by simple heating. The motivation sounds interesting, with some preliminary results reflecting the possible luminescence from obtained pyrolysis product of PET. However, owing to the lack of any piece of evidence to convince the formation of CDs, the whole work is just a simple demonstration that pyrolyzing PET at suitable temeprature for suitable time duration would lead to some luminescence. Therefore, the manuscript is far from being a self-consistent story giving a logical sequence from systematic experiment through comprehensive characterizations to well-established conclusions. Thre reviewer is firmly against its acceptance at its current status. Some other comments are as follows:
1. It is highly not imaginable that a manuscript discussing CDs is given without any SEM or TEM image of CDs. Is the resultant pyrolysis product of PET really CDs? No evidence is given. In fact, from the general pyrolysis knowledge, it

is hardly believable that such a process can result in CDs;
2. Emphasizing pyrolysis temperature around melting temperature is meaningless, because melting temperature reflects intermolecular behaviors, while decomposition temperature reflects molecular chain bond strength; by the way, it should be noticed that the characteristic temepratures in TG testing are highly dependent on heating rate, and TG curves only reflect weight loss, not able to reflect a decrease in molecular weight;
3. Figure 1b and 1c are highly questionable;
4. Just 'strong PL' would mean nothing if no further information such as quantum yield is given.

Reviewer #2: 1. Carbon dots (CDs) generally refer to the quasi-zero-dimensional fluorescent carbon-based nanomaterials with a size of less than 10 nm. However, in this manuscript, there are no transmission electron microscope (TEM) images of PET-CDs, thus, the authors cannot identify the synthesized material as CDs. The authors may have synthesized a kind of materials with fluorescence.
2. Aslo authors mentioned " Due to the severe aggregation-caused quenching, most CDs show no fluorescence in the solid state (B. Liu et al., 2021). This study obtained solid-state PET CDs with strong blue photoluminescence without aggregation." However, the author did not explain the reason for the solid-state luminescence of the prepared PET-CDs and more characterization is needed for further elucidation.
3. Using PET as raw material, various CDs have been extensively reported in the literature, and the results obtained in this work should be compared with that reported in other works.
4. Why does the TGA curve in Figure 1B decrease first and then increase? Why do PET-CDs prepared at different temperatures in Figure 2C exhibit small emission peaks within the range of 550-600nm? More explanations are required.
5. Please pay attention to writing standard of the manuscript, such as the space between numbers and units, the capitalization of abbreviations etc..

Reviewer #3: In this manuscript, the authors reported a one-step synthetic route to convert PET bottle waste into solid-state fluorescent carbon dots (CDs). Moreover, they discovered that PET-based CDs fabricated at 260 °C for 2.5 hours exhibit the highest fluorescence intensity. The work is very interesting, and offers a promising solution for plastic waste management. In my opinion, it can be accepted for publication after minor revisions.
(1) Since the preparation was based on the PET thermal decomposition with heating temperatures between 200 °C and 300 °C, it is suggested that the product might be "carbonized polymer dots" more than "carbon dots".
(2) The XRD patterns of the PET-CDs samples prepared at 240 oC and 260 oC respectively should be provided to see if there are any crystalline impurities inside them?
(3) What is the mass product yield of the PET-CDs in this work? Is this method can be used for large-scale preparation of CDs in the near future?

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3. Bukti permohonan perpanjangan batas waktu untuk revisi manuskrip
(28 Agustus 2023)

Revision of "Novel one-step synthesis of solid-state carbon dots by heating at around melting point of polyethylene terephthalate (PET) bottle plastic waste" is due soon

Mahardika Prasetya Aji <mahardika@mail.unnes.ac.id> Mon, Aug 28, 2023 at 3:51 PM
To: Piero Gardinali <gardinal@fiu.edu>

Dear Editor of Environmental Nanotechnology, Monitoring & Management

Thank you for your gently reminder. I hope this email finds you well. I am writing to respectfully request an extension for the due date of the revision submission for our manuscript with the ID ENMM-D-23-00365, titled " Novel one-step synthesis of solid-state carbon dots by heating at around melting point of polyethylene terephthalate (PET) bottle plastic waste." I am the corresponding author for this submission.

We greatly appreciate the feedback and constructive comments provided by the reviewers. These insights have been invaluable in refining our manuscript to meet the high standards set by Environmental Nanotechnology Monitoring and Management. However, considering the complexity of the revisions suggested and our commitment to producing a comprehensive and improved manuscript, we kindly request an extension of 20 days to finalize the revisions and ensure the quality of the work. We believe that the extra time will allow us to address all comments adequately and enhance the overall contribution of our paper.

We understand the importance of adhering to the publication schedule and assure you that we will make every effort to complete the revisions as promptly as possible within the extended timeframe. Your understanding and consideration of this request would be greatly appreciated. Please let us know if the extension can be granted.

Thank you very much for your time and consideration. We look forward to your response.

Best regards,

Dr. Mahardika Prasetya Aji
Department of Physics, Universitas Negeri Semarang
mahardika@mail.unnes.ac.id
[Quoted text hidden]

Revision of "Novel one-step synthesis of solid-state carbon dots by heating at around melting point of polyethylene terephthalate (PET) bottle plastic waste" is due soon

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Piero Gardinali <gardinal@fiu.edu> Mon, Aug 28, 2023 at 9:31 PM
To: Mahardika Prasetya Aji <mahardika@mail.unnes.ac.id>

No problem.

Please disregard the automated emails from the system.

I noted the request.

Thanks

Piero Gardinali

Piero R. Gardinali, PhD

Director, Freshwater Resources Division

Associate Director, the Institute of Environment, an FIU Preeminent Program

Professor
Department of Chemistry & Biochemistry

Florida International University
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North Miami, Florida, 33181

Phone: (305)348-6354 Fax:(305)348-3772
E-mail: gardinal@fiu.edu

4. Bukti submit revisi, respon dan revisi manuskrip

(19 September 2023)

(File : Revision Manuscript)

Mahardika Prasetya Aji <mahardika@mail.unnes.ac.id>

Confirming submission to Environmental Nanotechnology, Monitoring & Management

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Environmental Nanotechnology, Monitoring & Management <em@editorialmanager.com>
Tue, Sep 19, 2023 at 11:06 PM
Reply-To: "Environmental Nanotechnology, Monitoring & Management" <support@elsevier.com>
To: Mahardika Prasetya Aji <mahardika@mail.unnes.ac.id>

This is an automated message.

Manuscript Number: ENMM-D-23-00365R1

Novel one-step synthesis of solid-state carbonized polymer dots by heating at around melting point of polyethylene terephthalate (PET) bottle plastic waste

Dear Mr Prasetya Aji,

We have received the above referenced manuscript you submitted to Environmental Nanotechnology, Monitoring & Management.

To track the status of your manuscript, please log in as an author at https://www.editorialmanager.com/enmm/, and navigate to the "Revisions Being Processed" folder.

Thank you for submitting your revision to this journal.

Kind regards,
Environmental Nanotechnology, Monitoring & Management

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Environmental Nanotechnology, Monitoring & Management

Novel one-step synthesis of solid-state carbonized polymer dots by heating at around melting point of polyethylene terephthalate (PET) bottle plastic waste

--Manuscript Draft--

Manuscript Number:	ENMM-D-23-00365R1
Article Type:	Research Paper
Keywords:	carbonized polymer dots; solid-state fluorescence; polyethylene terephthalate; melting point
Corresponding Author:	Mahardika Prasetya Aji Semarang, Central Java Indonesia
First Author:	Mahardika Prasetya Aji
Order of Authors:	Mahardika Prasetya Aji
	Ita Rahmawati
	Aan Priyanto
	Putut Marwoto
Abstract:	Production of luminescent carbonized polymer dots (CPDs) in the solid state has been a crucial challenge due to their tendency to self-aggregate, leading to fluorescence quenching and limiting their applicability in the solid state. In this work, we present an environmentally friendly method for producing solid-state CPDs with high photoluminescence (PL) intensity by simple one-step heating method using waste PET bottle plastic as the raw material. Based on the PET thermal analysis, heating temperatures between 200 °C and 300 °C and heating duration were explored. Through systematic experimentation, we discovered that heating temperature and time play a crucial role in controlling PL intensity, ultraviolet-visible (UV-Vis) absorption, carbonization degree, and structure of CPDs. The carbonization of CPDs occurs when the heating temperature exceeds the PET melting point, resulting in strong PL characteristics in the range of 400 and 600 nm. However, when the temperature rises, the PL decreases as the number of oxygen-containing functional groups on the surface of CPDs increases. The optimal conditions for high PL intensity were 260 °C for 2.5 hours. Our one-step heating approach provides a cost-effective solution for recycling PET waste, offering promising potential for various applications.
Suggested Reviewers:	Yaoping Hu Ningbo University chem_yphu@yahoo.com
	Leah M Johnson GlaxoSmithKline Research Triangle Park leahjohnson@rti.org
	Bin Liu North University of China liubin@nuc.edu.cn
Opposed Reviewers:	
Response to Reviewers:	Authors’ Responses to Reviewers’ Comments on the Manuscript REVIEWER 1 #Comment 1: It is highly not imaginable that a manuscript discussing CDs is given without any SEM or TEM image of CDs. Is the resultant pyrolysis product of PET really CDs? No evidence is given. In fact, from the general pyrolysis knowledge, it is hardly believable that such a process can result in CDs. Authors' response: We thank the reviewer for the constructive consideration. TEM observations were conducted using a Hitachi HT7700 instrument. The TEM image and size distribution estimations have been included in the manuscript in Figure 4a on page 14 line 1. The estimations indicate that the CDs have a size of approximately 3 nm.

The manuscript revision regarding this additional measurement is written on page 12 line 10. References that are relevant to the size of CDs produced by PET are listed in Table 1 on page 18 line 2.

#Comment 2: Emphasizing pyrolysis temperature around melting temperature is meaningless, because melting temperature reflects intermolecular behaviors, while decomposition temperature reflects molecular chain bond strength; by the way, it should be noticed that the characteristic temperatures in TG testing are highly dependent on heating rate, and TG curves only reflect weight loss, not able to reflect a decrease in molecular weight.
Authors' response: The given statement is highly significant and offers insights into the concepts of melting temperature and decomposition temperature. Although the melting point only refers to intermolecular interactions, it can be useful in determining the thermal decomposition temperature. The melting point is a simple indicator to consider before creating CDs. In the present study, it is observed that temperatures slightly exceeding the melting point trigger thermal decomposition in PET. At temperatures in excess of the melting temperature, the nucleus in polymer is unstable due to the thermal atomic vibrations that tend to disrupt the ordered molecular arrangements. After nucleation and during the growth stage, nuclei grow by the continued ordering and alignment of additional molecular chain segments.
The significance of addressing the melting point was also noted by Bagheri et al. (2017). CDs composed of citric acid were produced under thermal decomposition conditions, i.e., between 160 and 220 C. This temperature number is slightly higher than the melting point of citric acid, which is 153 oC.
The statement that the characteristics of the DTA and TG curves depend on the heating rate is very appropriate. The retest results for DTA, TG and DTGA, as depicted in Figures 1a-c, illustrate the different weight loss curves observed when employing heating rates of 20 °C/min and 50 °C/min. It is understood that the curves in Figures 1b and 1c represent weight loss rather than a decrease in molecular weight. Regarding this, page wording revisions have been made on page 6 line 19.

#Comment 3: Figure 1b and 1c are highly questionable.
Authors' response: We appreciate the reviewer criticism. Due to the error in the previous curve, new measurements were performed for DTA, TG, and DTGA. The measurements were conducted at 20 oC/min and 50 oC/min heating rates. The appropriate results have been achieved and are shown in Figures 1a-c on page 7 line 12 of the text.

#Comment 4: Just 'strong PL' would mean nothing if no further information such as quantum yield is given.
Authors' response: We express our regrets for our inability to conduct these measurements. This device is currently not available in research institutions or universities in our country.

REVIEWER 2
#Comment 1: Carbon dots (CDs) generally refer to the quasi-zero-dimensional fluorescent carbon-based nanomaterials with a size of less than 10 nm. However, in this manuscript, there are no transmission electron microscope (TEM) images of PET-CDs, thus, the authors cannot identify the synthesized material as CDs. The authors may have synthesized a kind of materials with fluorescence.
Authors' response: Thanks to the reviewer suggestions. TEM measurement was conducted using a Hitachi HT7700 instrument. The TEM image and size distribution estimations have been included in the manuscript in Figure 4a on page 14 line 1. The estimations indicate that the CDs have a size of approximately 3 nm. The manuscript revision regarding this additional measurement is written on page 12 line 10. References that are relevant to the size of CDs produced by PET are listed in Table 1 on page 18 line 2.

#Comment 2: Also authors mentioned " Due to the severe aggregation-caused quenching, most CDs show no fluorescence in the solid state (B. Liu et al., 2021). This study obtained solid-state PET CDs with strong blue photoluminescence without aggregation." However, the author did not explain the reason for the solid-state luminescence of the prepared PET-CDs and more characterization is needed for further elucidation.

Authors' response: We thank the reviewer for the constructive comments. This study obtained solid-state PET-CPDs with strong blue photoluminescence without aggregation. The observed phenomenon can be attributed to the presence of a large number of surface PET chains surrounding the core of CPDs, which effectively prevents π-π interactions. Consequently, the quenching process induced by aggregation is blocked. In addition, it is worth noting that PET-CPDs exhibit strong hydrophobic characteristics in contrast to many other CPDs that possess hydrophilic surfaces. This characteristic limits the electrostatic interaction and particle attraction of CPDs (Ru et al., 2022; Yang et al., 2019).
In order to investigate the features of this aggregation, transmission electron microscopy (TEM) analysis was conducted, revealing that the particles of the CDs are spherical in shape, uniform and well distributed without aggregation. This explanation has been added to the manuscript on page 12 line 11.

#Comment 3: Using PET as raw material, various CDs have been extensively reported in the literature, and the results obtained in this work should be compared with that reported in other works.
Authors' response: Thanks for the reviewer’s recommendation. In accordance with your suggestion, a comparison of the results of this work with those of several other research is provided in Table 1 on page 18 line 1.

#Comment 4: Why does the TGA curve in Figure 1B decrease first and then increase? Why do PET-CDs prepared at different temperatures in Figure 2C exhibit small emission peaks within the range of 550-600nm? More explanations are required.
Authors' response: We thank the reviewer for pointing this out. Due to the error in the previous curve, new measurements were performed for DTA, TG, and DTGA. The retest results have been re-presented in Figure 1b. The weight loss curve exhibits a consistent decline as the temperature ranges from 380°C to 500°C. Results from two measurements conducted at heating rates of 20 °C/min and 50 °C/min indicate that the curve does not exhibit any further increase subsequent to the observed weight loss.
It is apparent that the photoluminescence (PL) spectrum has a little peak at a wavelength of 575 nm. The observed peak suggests that PET-CPDs exhibit multiple emission centers, with the additional emission usually due to the presence of polycyclic aromatic hydrocarbons of varying sizes. This is in comparison with the conjugated sp2 domains formed during the dehydration of the polymeric structure. We have added this explanation on page 9 line 11.

#Comment 5: Please pay attention to writing standard of the manuscript, such as the space between numbers and units, the capitalization of abbreviations etc.
Authors' response: Thanks for the reviewer comments. The use of standard writing has been employed.

REVIEWER 3
#Comment 1: Since the preparation was based on the PET thermal decomposition with heating temperatures between 200 °C and 300 °C, it is suggested that the product might be "carbonized polymer dots" more than "carbon dots"
Authors' response: We thank the reviewer for the suggestion. In the manuscript, we have used the term carbonized polymer dots (CPDs) to denote the final product.

Comment 2: The XRD patterns of the PET-CDs samples prepared at 240 oC and 260 oC respectively should be provided to see if there are any crystalline impurities inside them?
Authors' response: Thanks to the reviewer considerations. Following your suggestion, we have added XRD diffractograms that are presented in Figure 4c on page 14 line 1. The diffraction pattern obtained from the PET sample exhibits characteristics indicative of a semicrystalline structure. The effect of thermal treatment generates new peaks, indicating the presence of PET crystal impurities.

#Comment 3: What is the mass product yield of the PET-CDs in this work? Is this method can be used for large-scale preparation of CDs in the near future?
Authors' response: We thank the reviewer for pointing this out. The mass of CPDs produced in a single manufacturing process is 0.028 grams. Because the manufacturing temperature is slightly higher than the melting point and significantly lower than the weight loss temperature, the entire PET material can be converted into

	PET-CPDs. Due to the relatively low temperature employed, the utilized method has great potential for large-scale production of CPDs. The results of this work provide valuable information because the preparation of CPDs becomes more effective.

September 19, 2023

To: Editor-in-chief of *Environmental Nanotechnology, Monitoring & Management*

Dear **Piero Gardinali, PhD**,

Please find enclosed our revised manuscript entitled '**Novel one-step synthesis of solid-state carbonized polymer dots by heating at around melting point of polyethylene terephthalate (PET) bottle plastic waste**', by Mahardika Prasetya Aji, Ita Rahmawati, Aan Priyanto, Putut Marwoto, which we are submitting for publication in *Environmental Nanotechnology, Monitoring & Management* as a paper.

We would like to express our sincere gratitude for the time and effort that you have dedicated to providing us with valuable feedback on our manuscript. We are truly appreciative of the reviewers for their insightful comments on our work, which have been valuable in helping us to improve the manuscript.

We have made every effort to carefully consider and respond to all the comments and questions raised by the reviewers and have made appropriate adjustments to the revised manuscript in response. We hope these revisions have strengthened the overall quality and clarity of the manuscript.

Sincerely yours,

Dr. Mahardika Prasetya Aji, M.Si.
Associate Professor
Department of Physics, Faculty of Mathematics and Natural Sciences,
Universitas Negeri Semarang
Jalan Sekaran No. 10, Semarang, Indonesia.
E-mail: mahardika@mail.unnes.ac.id

Authors' Responses to Reviewers' Comments on the Manuscript

Title: **Novel one-step synthesis of solid-state carbonized polymer dots by heating at around melting point of polyethylene terephthalate (PET) bottle plastic waste**

Authors: Mahardika Prasetya Aji, Ita Rahmawati, Aan Priyanto, and Putut Marwoto

Dear Editor and Reviewer,

We would like to express our sincere gratitude for the time and effort that you have dedicated to providing us with valuable feedback on our manuscript. We are truly appreciative of the reviewers for their insightful comments on our work, which have been valuable in helping us to improve the manuscript.

We have made every effort to carefully consider and respond to all the comments and questions raised by the reviewers and have made appropriate adjustments to the revised manuscript in response (indicated by red color). We hope these revisions have strengthened the overall quality and clarity of the manuscript.

Please find enclosed a response to the reviewer comments and concerns, which we hope will address any remaining issues and demonstrate our commitment to producing a high-quality publication.

Sincerely,
Corresponding Author,
Dr. Mahardika Prasetya Aji, M.Si.

Reviewers' comments	**Responses**
Reviewer 1	
1. It is highly not imaginable that a manuscript discussing CDs is given without any SEM or TEM image of CDs. Is the resultant pyrolysis product of PET really CDs? No evidence is given. In fact, from the general pyrolysis knowledge, it is hardly believable that such a process can result in CDs;	We thank the reviewer for the constructive consideration. TEM observations were conducted using a Hitachi HT7700 instrument. The TEM image and size distribution estimations have been included in the manuscript in Figure 4a on page 14 line 1. The estimations indicate that the CDs have a size of approximately 3 nm. The manuscript revision regarding this additional measurement is written on page 12 line 10. References that are relevant to the size of CDs produced by PET are listed in Table 1 on page 18 line 2.

Reviewers' comments	Responses
2. Emphasizing pyrolysis temperature around melting temperature is meaningless, because melting temperature reflects intermolecular behaviors, while decomposition temperature reflects molecular chain bond strength; by the way, it should be noticed that the characteristic temperatures in TG testing are highly dependent on heating rate, and TG curves only reflect weight loss, not able to reflect a decrease in molecular weight;	The given statement is highly significant and offers insights into the concepts of melting temperature and decomposition temperature. Although the melting point only refers to intermolecular interactions, it can be useful in determining the thermal decomposition temperature. The melting point is a simple indicator to consider before creating CDs. In the present study, it is observed that temperatures slightly exceeding the melting point trigger thermal decomposition in PET. At temperatures in excess of the melting temperature, the nucleus in polymer is unstable due to the thermal atomic vibrations that tend to disrupt the ordered molecular arrangements. After nucleation and during the growth stage, nuclei grow by the continued ordering and alignment of additional molecular chain segments. The significance of addressing the melting point was also noted by Bagheri et al. (2017). CDs composed of citric acid were produced under thermal decomposition conditions, i.e., between 160 and 220 C. This temperature number is slightly higher than the melting point of citric acid, which is 153 ºC. The statement that the characteristics of the DTA and TG curves depend on the heating rate is very appropriate. The retest results for DTA, TG and DTGA, as depicted in Figures 1a-c, illustrate the different weight loss curves observed when employing heating rates of 20 °C/min and 50 °C/min. It is understood that the curves in Figures 1b and 1c represent weight loss rather than a decrease in molecular weight. Regarding this, page wording revisions have been made on page 6 line 19.
3. Figure 1b and 1c are highly questionable;	We appreciate the reviewer criticism. Due to the error in the previous curve, new measurements were performed for DTA, TG, and DTGA. The measurements were conducted at 20 ºC/min and 50 ºC/min heating rates. The appropriate results have been achieved and are shown in Figures 1a-c on page 7 line 12 of the text.

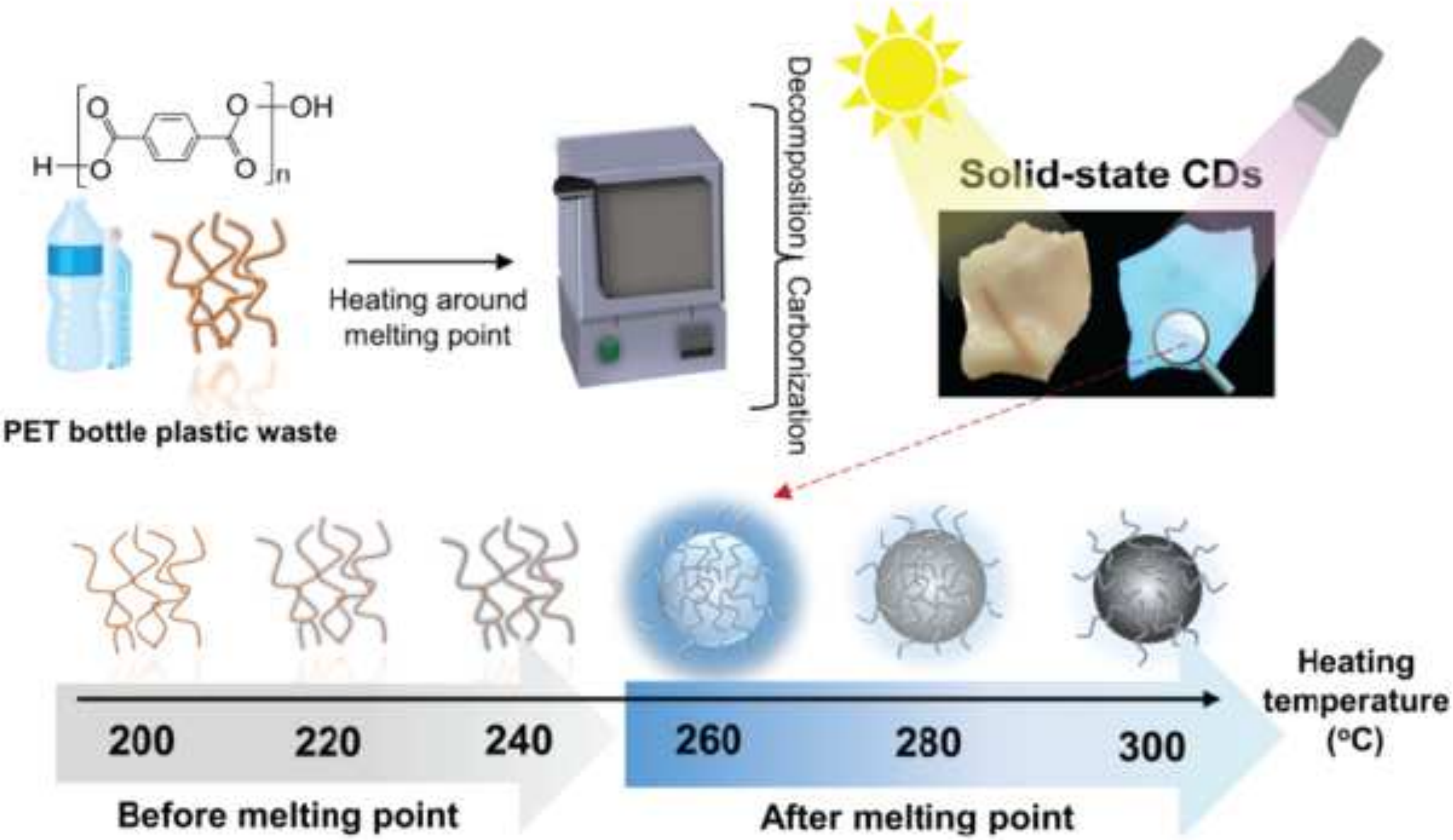
Reviewers' comments	Responses
4. Just 'strong PL' would mean nothing if no further information such as quantum yield is given.	We express our regrets for our inability to conduct these measurements. This device is currently not available in research institutions or universities in our country.
Reviewer 2	
1. Carbon dots (CDs) generally refer to the quasi-zero-dimensional fluorescent carbon-based nanomaterials with a size of less than 10 nm. However, in this manuscript, there are no transmission electron microscope (TEM) images of PET-CDs, thus, the authors cannot identify the synthesized material as CDs. The authors may have synthesized a kind of materials with fluorescence.	Thanks to the reviewer suggestions. TEM measurement was conducted using a Hitachi HT7700 instrument. The TEM image and size distribution estimations have been included in the manuscript in Figure 4a on page 14 line 1. The estimations indicate that the CDs have a size of approximately 3 nm. The manuscript revision regarding this additional measurement is written on page 12 line 10. References that are relevant to the size of CDs produced by PET are listed in Table 1 on page 18 line 2.
2. Also authors mentioned " Due to the severe aggregation-caused quenching, most CDs show no fluorescence in the solid state (B. Liu et al., 2021). This study obtained solid-state PET CDs with strong blue photoluminescence without aggregation." However, the author did not explain the reason for the solid-state luminescence of the prepared PET-CDs and more characterization is needed for further elucidation.	We thank the reviewer for the constructive comments. This study obtained solid-state PET-CPDs with strong blue photoluminescence without aggregation. The observed phenomenon can be attributed to the presence of a large number of surface PET chains surrounding the core of CPDs, which effectively prevents π-π interactions. Consequently, the quenching process induced by aggregation is blocked. In addition, it is worth noting that PET-CPDs exhibit strong hydrophobic characteristics in contrast to many other CPDs that possess hydrophilic surfaces. This characteristic limits the electrostatic interaction and particle attraction of CPDs (Ru et al., 2022; Yang et al., 2019). In order to investigate the features of this aggregation, transmission electron microscopy (TEM) analysis was conducted, revealing that the particles of the CDs are spherical in shape, uniform and well distributed without aggregation. This explanation has been added to the manuscript on page 12 line 11.
3. Using PET as raw material, various CDs have been extensively reported in the literature, and the results obtained in this work should be compared with that reported in other works.	Thanks for the reviewer's recommendation. In accordance with your suggestion, a comparison of the results of this work with those of several other research is provided in Table 1 on page 18 line 1.

Reviewers' comments	Responses
4. Why does the TGA curve in Figure 1B decrease first and then increase? Why do PET-CDs prepared at different temperatures in Figure 2C exhibit small emission peaks within the range of 550-600nm? More explanations are required.	We thank the reviewer for pointing this out. Due to the error in the previous curve, new measurements were performed for DTA, TG, and DTGA. The retest results have been re-presented in Figure 1b. The weight loss curve exhibits a consistent decline as the temperature ranges from 380°C to 500°C. Results from two measurements conducted at heating rates of 20 °C/min and 50 °C/min indicate that the curve does not exhibit any further increase subsequent to the observed weight loss. It is apparent that the photoluminescence (PL) spectrum has a little peak at a wavelength of 575 nm. The observed peak suggests that PET-CPDs exhibit multiple emission centers, with the additional emission usually due to the presence of polycyclic aromatic hydrocarbons of varying sizes. This is in comparison with the conjugated sp^2 domains formed during the dehydration of the polymeric structure. We have added this explanation on page 9 line 11.
5. Please pay attention to writing standard of the manuscript, such as the space between numbers and units, the capitalization of abbreviations etc..	Thanks for the reviewer comments. The use of standard writing has been employed.
Reviewer 3	
1. Since the preparation was based on the PET thermal decomposition with heating temperatures between 200 °C and 300 °C, it is suggested that the product might be "carbonized polymer dots" more than "carbon dots".	We thank the reviewer for the suggestion. In the manuscript, we have used the term carbonized polymer dots (CPDs) to denote the final product.
2. The XRD patterns of the PET-CDs samples prepared at 240 °C and 260 °C respectively should be provided to see if there are any crystalline impurities inside them?	Thanks to the reviewer considerations. Following your suggestion, we have added XRD diffractograms that are presented in Figure 4c on page 14 line 1. The diffraction pattern obtained from the PET sample exhibits characteristics indicative of a semicrystalline structure. The effect of thermal treatment generates new peaks, indicating the presence of PET crystal impurities.
3. What is the mass product yield of the PET-CDs in this work? Is this method can be used for large-scale preparation of CDs in the near future?	We thank the reviewer for pointing this out. The mass of CPDs produced in a single manufacturing process is 0.028 grams. Because the manufacturing temperature is slightly

Reviewers’ comments	Responses
	higher than the melting point and significantly lower than the weight loss temperature, the entire PET material can be converted into PET-CPDs. Due to the relatively low temperature employed, the utilized method has great potential for large-scale production of CPDs. The results of this work provide valuable information because the preparation of CPDs becomes more effective.

Highlights

- Environmentally friendly CDs produced from waste PET bottle plastic by simple heating method.
- Heating temperature around its melting point and duration crucial for controlling PL intensity, UV-Vis absorption, and structure of PET-CDs.
- Optimum conditions for high PL intensity found at 260 °C for 2.5 hours.
- Solution for recycling plastic waste and cost-effective production of solid-state fluorescent CDs.


H
O
O
O
O
OH
n
PET bottle plastic waste
Heating around melting point
Decomposition
Carbonization
Solid-state CDs
200
220
240
260
280
300
Heating temperature (°C)
Before melting point
After melting point

Novel one-step synthesis of solid-state carbonized polymer dots by heating at around melting point of polyethylene terephthalate (PET) bottle plastic waste

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Abstract

Production of luminescent carbonized polymer dots (CPDs) in the solid state has been a crucial challenge due to their tendency to self-aggregate, leading to fluorescence quenching and limiting their applicability in the solid state. In this work, we present an environmentally friendly method for producing solid-state CPDs with high photoluminescence (PL) intensity by simple one-step heating method using waste PET bottle plastic as the raw material. Based on the PET thermal analysis, heating temperatures between 200 °C and 300 °C and heating duration were explored. Through systematic experimentation, we discovered that heating temperature and time play a crucial role in controlling PL intensity, ultraviolet-visible (UV-Vis) absorption, carbonization degree, and structure of CPDs. The carbonization of CPDs occurs when the heating temperature exceeds the PET melting point, resulting in strong PL characteristics in the range of 400 and 600 nm. However, when the temperature rises, the PL decreases as the number of oxygen-containing functional groups on the surface of CPDs increases. The optimal conditions for high PL intensity were 260 °C for 2.5 hours. Our one-step heating approach provides a cost-effective solution for recycling PET waste, offering promising potential for various applications.

Keywords: carbonized polymer dots, solid-state fluorescence, polyethylene terephthalate, melting point

1. Introduction

Plastic bottles are commonly encountered packaging materials due to their versatility, durability, and low cost (Benyathiar et al., 2022; Rodríguez-Hernández et al., 2019). It is expected that around 62% of all plastic bottles have been made from polyethylene terephthalate (PET) (Amirudin et al., 2022; Becerril-Arreola and Bucklin, 2021; Zhang et al., 2020). Nowadays, it is very convenient to use PET bottles as single-use beverage packaging. Consequently, disposable PET bottles accumulate as waste and become a significant environmental concern due to their non-biodegradable properties. The biodegradation of PET waste can take up to 500 years and releases harmful toxins into the water and soil, posing risks to human health and biodiversity (Becerril-Arreola and Bucklin, 2021; Gao et al., 2022; Ghosh and Das, 2021). Incineration is a common method for disposing of PET waste, but it contributes to air pollution and releases high CO_2 emissions that exacerbate greenhouse effects and climate change (Song et al., 2019; Yin et al., 2021). Thus, there is a pressing need for a more environmentally friendly method to increase the value of these waste materials. Recently, alternative methods have been developed to process PET wastes as a promising source for synthesis of carbon-based nanomaterial, such as carbon dots (Ghosh and Das, 2021; Hu et al., 2021, 2019; Johnson et al., 2021; Rodríguez-Hernández et al., 2019).

Carbonized polymer dots (CPDS) belong to the class of carbon dots and have emerged as a very promising group of zero-dimensional carbon-based nanomaterial that have gained significant attention for their outstanding properties, such as chemical stability, low toxicity, and good optical stability, showing promising potential for many advanced applications (Bagheri et al., 2017; Mansuriya and Altintas, 2021; Song et al., 2019). CPDs have a carbon/polymer hybrid structure with a carbon core, abundant surface functional groups and short polymer chains, which are reserved owing to a low or incomplete carbonization degree (Wang et al., 2021; Xia et al., 2019a). Their characteristics and states can be tunable depending on their application (Mansuriya and Altintas, 2021). In recent years, there has been an increased demand for solid-state CPDs in optoelectronic devices, sensors, fingerprint identification, fluorescent ink, security label, and others (Jin et al., 2020; Singaravelu et al., 2021; Wang et al., 2020). However, solid-state CPDs always suffer from fluorescent quenching due to direct π-π interactions or excessive fluorescence resonance energy transfer (Ren et al., 2021; Singaravelu et al., 2021; Wang et al., 2020), which seriously limits their application in solid-state emissions. Currently, to obtain solid-state fluorescent CPDs, many efforts have been made usually using two main strategies: (i) the synthesis of fluorescent self-quenching-resistant solid-state CPDs, and (ii) blending CPDs with polymers materials to restrict intermolecular motions (Ren et al., 2021; Singaravelu et al., 2021). The second strategy, however, involves a complicated fabrication process and can reduce the optical performance of CPDs (Yoo et al., 2019). Therefore, there is need for the development of solid-state CPDs that are substantially resistant to self-quenching.

Plastic-based CPDs are a great candidate among the various solid-state CPDs since they naturally have hydrophobic qualities, as highlighted by Yin et al (Song et al., 2019). PET plastic-based CPDs, in particular, may also show potential, given their similar properties. Although the final product is liquid-state carbon dots, several studies of PET-based carbon dots have been performed using a two-step synthesis method. Ghosh and Das reported the heating of PET to high temperatures at the first step of synthesis, producing a dark and dry powder resembling carbon black (Ghosh and Das, 2021). Similarly, Hu et al. also conducted a two-step synthesis with the heating of PET at the first step (Hu et al., 2021). However, if the carbonization temperature is optimized, solid-state CPDs with high fluorescent can be yielded without requiring a second synthesis step. As Bagheri and his coworkers reported, the optimum carbonization degree in the synthesis carbon dots was affected by melting point of starting material during heating process. The photoluminescent behavior of carbon dots strongly depends on the temperature of heating during synthesis (Bagheri et al., 2017). To the best of our knowledge, there have been no reports on the investigation of PET-based CPDs in a solid state. Specifically, synthesis according to the thermal decomposition of PET has not been considered.

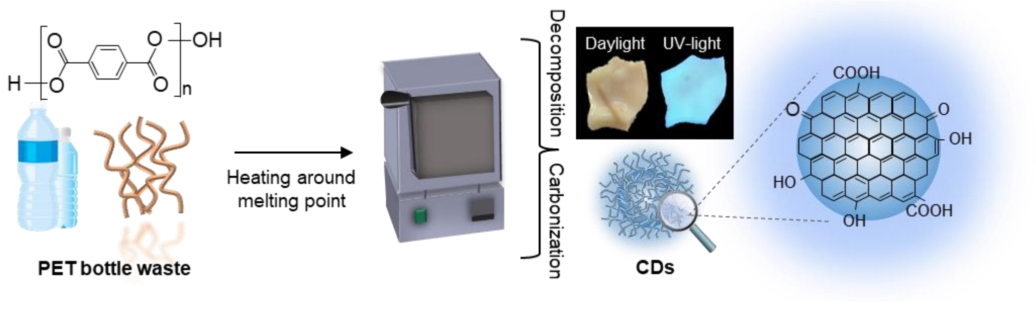
This study reported a simple synthesis route for producing solid-state CPDs from PET plastic waste. An experiment plan was arranged to gather the maximum information possible regarding the formation of these materials and the impact of synthesis conditions on their optical and chemical composition. The heating temperatures were investigated around the melting point of PET because carbon chains in the polymer decompose at temperatures above the melting point, which may lead to nucleation processes generating carbon cores. This study opens up a new understanding of the melting temperature as a critical point for synthesizing CPDs which only a few researchers have pointed out. In addition, the synthesis process does not require toxic, corrosive, or expensive solvents which are typically employed in synthesizing CPDs. The production of solid-state fluorescent CPDs from PET plastic waste increases the added value of PET waste and opens opportunities for future research in plastic waste management.

2. Material and Methods

Synthesis of CPDs. The solid-state CPDs were prepared by a one-step heating method using PET bottle waste as a carbon source. First, a waste PET bottle was collected and washed subsequently using water. The dried PET bottle was cut into small flakes and, afterward, transferred in a crucible for air oxidation in a muffle furnace at various temperatures ranging from 200 ^{o}C to 300 ^{o}C for 2.5 hours. The optimal temperature was determined to be 240 °C and was selected for the heating durations of 1 hour to 3 hours. The resulting solid-state product was collected and then characterized.

Characterization. UV-visible absorption spectra were recorded using a BMG Labtech Fluostar Omega spectrometer. Fluorescence measurements were carried out using a Cary Eclipse MY14440002 spectrofluorometer. Integrated fluorescence intensity is the area under the PL curve in the wavelength range from 400 to 650 nm. Fourier Transform Infrared (FTIR) spectra were recorded for powder CPDs using the Perkin-Elmer Spectrum Version 10.03.06 with an ATR attachment. Thermogravimetric analysis (TGA) was performed using a STA7300 Hitachi with a heating rate of 20 °C/min and 50 ^{o}C/min. Raman spectroscopy was measured using Horiba LabRAM HR Evolution Laser 785 nm. XRD measurements were performed using a Rigaku Smart Lab X-Ray diffractometer with CuKα radiation at a wavelength of $\lambda = 1.540\ \dot{A}$ to determine the crystalline phase of the synthesized samples. The size of the CPDs were investigated using TEM measurements performed on a HT7700 Hitachi at 80 kV.

3. Results and Discussion



Scheme 1. Mechanism for the preparation of solid-state CPDs based on PET bottle waste

The solid-state CPDs were synthesized from PET bottle waste using a simple heating process in a muffle furnace without any additional chemicals (Scheme 1). In preparing CPDs using the heating method, the PET chains were decomposed, followed by carbonization and then solid-state CPDs were formed. In this study, a systematic synthesis study was conducted by setting the synthesis temperature at around the melting point of PET and varying the heating duration to get the maximum information possible. The DTA of PET bottle waste (Fig. 1a) showed a strong endothermic peak at around 250 ^{o}C, implying a melting point of PET. Melting occurs when atomic vibrations are vigorous enough to rupture large numbers of atomic bonds in PET. For polymers, upon cooling through the melting temperature, nuclei form wherein small regions of the tangled and random molecules become ordered and aligned. At temperatures in excess of the melting temperature, these nuclei are unstable due to the thermal atomic vibrations that tend to disrupt the ordered molecular arrangements. After nucleation and during the growth stage, nuclei grow through the continued ordering and alignment of additional molecular chain segments (Callister, 2001). On the other hand, the TGA curve (Fig 1b and c) confirmed a decrease in weight loss, with the thermal degradation of PET onsets at 380 ^{o}C (at heating rate 20 ^{o}C/min) and at 395 ^{o}C (at heating rate 50 ^{o}C/min). The results also reveal that the heating rate affects the DTA and TGA test results, however the difference is not significant.

Furthermore, FTIR analysis shows that PET plastic bottles (Fig. 2d) showed the presence of broad molecular groups consisting of carbon, hydrogen, and oxygen. The C-H stretching vibration modes appear in the region 3000-2825 cm^{-1} that refer to the functional groups such as alkyl, alkanal, alkyne, alkene, and arene. The C-H bending mode of vibration, which has weaker bond strength than their stretching modes, appears in the region 924-808 cm^{-1} and 573 cm^{-1} (Prasad et al., 2011). The absorption at 3412 cm^{-1} is assigned to the O-H stretching at the end group of the PET molecule chain. The C=O stretching and the aromatic skeleton stretching bands were observed at 1730 and 1614 cm^{-1}, respectively (Torres-Huerta et al., 2016).

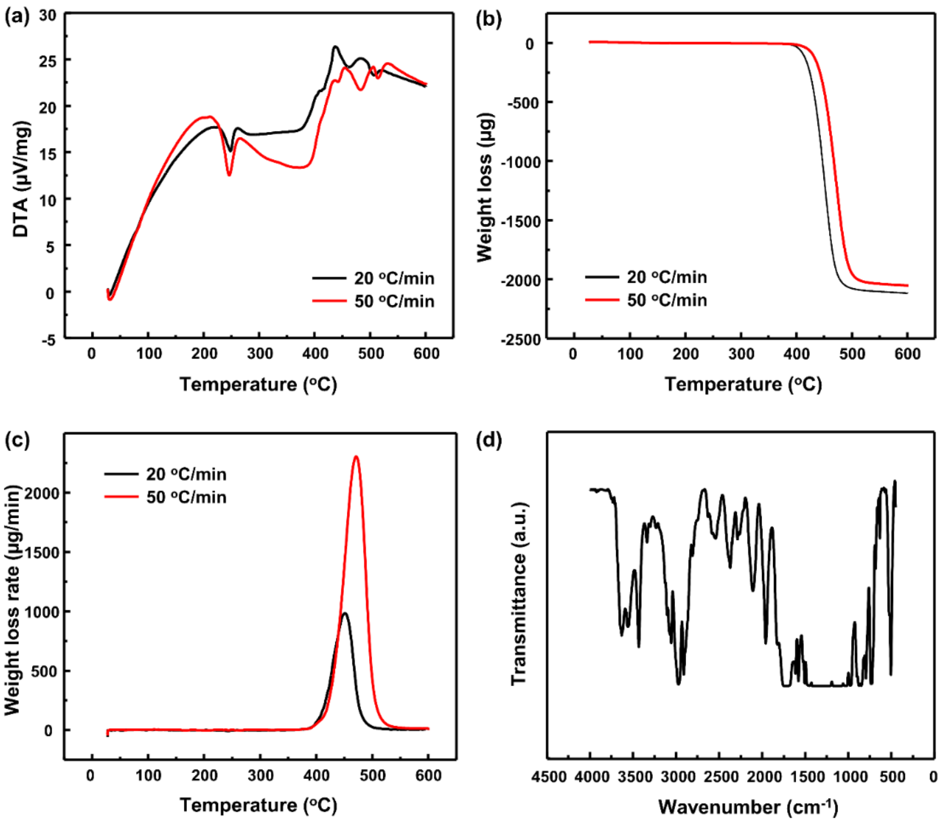


Figure 1. Starting material (PET bottle waste) analysis: (a) differential thermal analysis (DTA), (b) thermogravimetric analysis (TGA), (c) derivative TGA (DTGA), and (d) Fourier Transform Infrared Spectroscopy (FTIR).

The distribution of the samples with different heating temperatures is shown in Fig 2a. Physically, the samples heated at temperatures ranging from 200 to 240 ^{o}C (below the melting point) remained transparent but exhibited increased brittleness and shrinkage compared to the unheated sample. On the other hand, the samples heated over the melting point (260-300 ^{o}C) showed significant physical alteration, such as becoming opaque, extremely brittle, and undergoing a color from light brown to dark brown. Moreover, under UV light, the results revealed that samples heated between 200-240 ^{o}C exhibited no luminescence. Meanwhile, samples of 260-300 ^{o}C showed luminescence, with samples of 260 ^{o}C having the brightest luminescence. This result indicated that determining the synthesis temperature around the melting point is one of the most crucial variables in producing CPDs with excellent luminescence.

The UV-Vis absorption spectra of the samples with varying synthesis temperatures are depicted in Fig 2b. Samples at 200-240 ^{o}C were not characterized due to their high stickiness and very weak luminescence. The UV-Vis spectra displayed absorption in the UV region of 220-300 nm. A stronger peak was observed at 240 nm with a shoulder at 280 nm originating from π-π* transition of C-C and C=C in aromatic rings of the carbon core and n-π* transition of oxygen-related bonds (C=O and C-O) on the surface state of CPDs, respectively (Ding et al., 2016; Y. Y. Liu et al., 2021). In the case of the 260 °C sample (CPDs-260), the peak at 240 nm was higher than in the other CPDs, indicating that it has stronger absorption properties. This result supports the conclusion that the synthesis temperature has a significant effect on the absorption properties of the synthesized CPDs (Zhang et al., 2016).

The PL spectra of the as-synthesized CPDs at different temperatures are depicted in Fig 2c. Upon excitation at 360 nm, PL intensity also shows a similar trend as the 240 nm peak of CPDs absorption intensity, suggesting the luminescence of solid-state PET-based CPDs may originate from the π-π* bond transition in the carbon core. Widely proposed luminescence mechanisms of CPDs originate from the conjugated π-domain within the graphitic carbon core, the surface state, or the molecular state of CPDs (Ai et al., 2021; Xia et al., 2019b). Here, the emission of PET-based CPDs belonged to the core-state luminescence mechanism category. Under 360 nm irradiation, the luminescence of solid-state CPDs centered at 450 nm, indicating blue color (in line with the physical appearance Fig. 2a). Additionally, it is apparent that the photoluminescence (PL) spectrum has a little peak at a wavelength of 575 nm. The observed peak suggests that PET-CPDs exhibit multiple emission centers, with the additional emission usually due to the presence of polycyclic aromatic hydrocarbons of varying sizes. This is in comparison with the conjugated sp^2 domains formed during the dehydration of the polymeric structure (Shamsipur et al., 2018).

As shown in Figure 2d, the integrated fluorescence intensity is derived from the area under the PL curve in the 400 to 650 nm range. The PL intensity changes with heating temperature, and CPDs-260 has the highest intensity. However, the PET-based CPDs emit less light and look black when the heating temperature is quite higher than the melting point, indicating that carbonization occurs during the formation of CPDs. Due to the severe aggregation-caused quenching, most CPDs show no fluorescence in the solid state (B. Liu et al., 2021). This study obtained solid-state PET-CPDs with strong blue photoluminescence without aggregation. The observed phenomenon can be attributed to the presence of a large number of surface PET chains surrounding the core of CPDs, which effectively prevents π-π interactions. Consequently, the quenching process induced by aggregation is blocked. In addition, it is worth noting that PET-CPDs exhibit strong hydrophobic characteristics, in contrast to many other CPDs that possess hydrophilic surfaces. This characteristic limits the electrostatic interaction and particle attraction of CPDs (Ru et al., 2022; Yang et al., 2019).

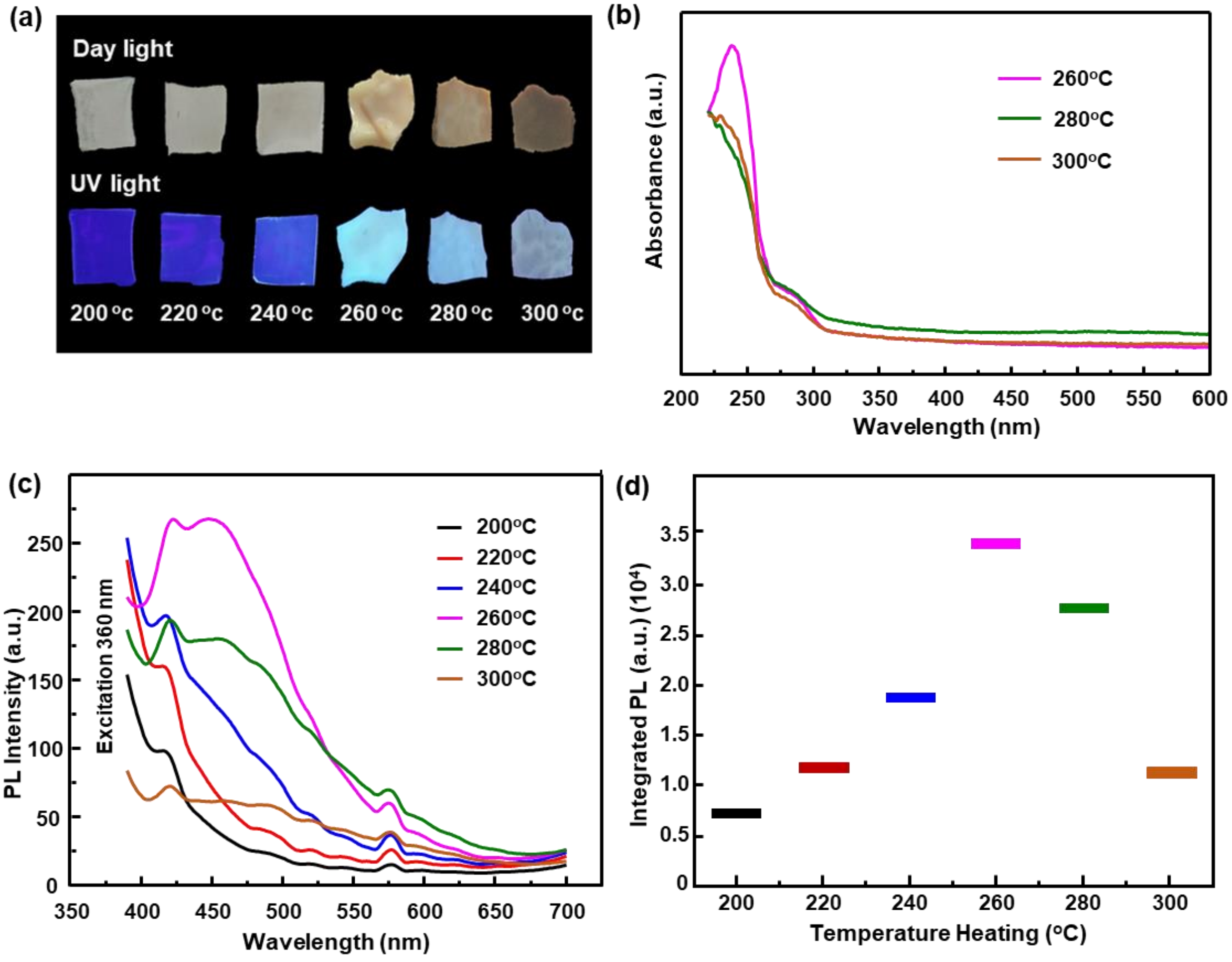


Figure 2. (a) Solid-state PET-based CPDs under visible light (up) and UV radiation (down) over heating temperature variation, (b) UV-Vis absorption of solid-state PET-based CPDs, (c) PL

spectra of the solid-state PET-based CPDs samples under 360 nm, (d) integrated PL of spectra PL from 400 to 650 nm wavelength.

As shown in Fig. 3, Fourier Transform Infrared (FTIR) was performed to determine the composition of the PET-CPDs. The FTIR results confirmed the presence of different functional groups in the synthesized CPDs, including oxygen, hydrogen, and carbon (Fig. 3a). Compared to the FTIR results of untreated PET, some of the PET composition significantly changed after heating above the melting point, indicating decomposition occurred during the heating process (Fig 3a). The absorbance at 1430 cm^{-1} changed significantly, indicating a C-O group presence. The higher the temperature, the more energy the sample will attach to ambient oxygen. In addition, changes at 1670 cm^{-1} were observed, indicating conjugated C=C and C=O bonds (Fig. 3b). The untreated PET showed a C=C bond from the aromatic skeleton at 1610 cm^{-1} and the C=O bond from the carbonyl at 1720 cm^{-1}. However, when the PET was heated above the melting point, the C=C and C=O frequencies shifted and were no longer distinguishable, moving to 1660 cm^{-1} and indicating conjugation of the carbonyl group with a C=C double bond. The presence of the C=C and C=O bond signatures suggests forming a π-conjugated system as CPDs core structure (Permatasari et al., 2021). This conjugation bond plays a role in the CPDs photoluminescence process, which is related to the energy gap (Permatasari et al., 2021; Semeniuk et al., 2019; Wang et al., 2017). The results of this study demonstrate that temperatures above the melting point can lead to the formation of conjugate bonds in the aromatic skeleton of the PET-based CPDs, resulting in solid luminescence. However, CPDs-280 and CPDs-300 have lower luminescence intensity (as previously demonstrated in Fig 2c) due to a large number of attached oxygen bonds. These oxygen-containing groups lead to non-radiative coupling of electron-hole pairs that suppress CPDs PL (Ai et al., 2021). In addition, as depicted in Fig. 3c, PET-CPDs feature C-H sp^3 bond vibrations between 3000 to 2800 cm^{-1}, suggesting the carbon core of the PET-CPDs. In contrast, untreated PET possessed C-H sp^2 bonds that vanished upon heating, indicating that heating at temperatures above the melting point decomposed the original PET structure.

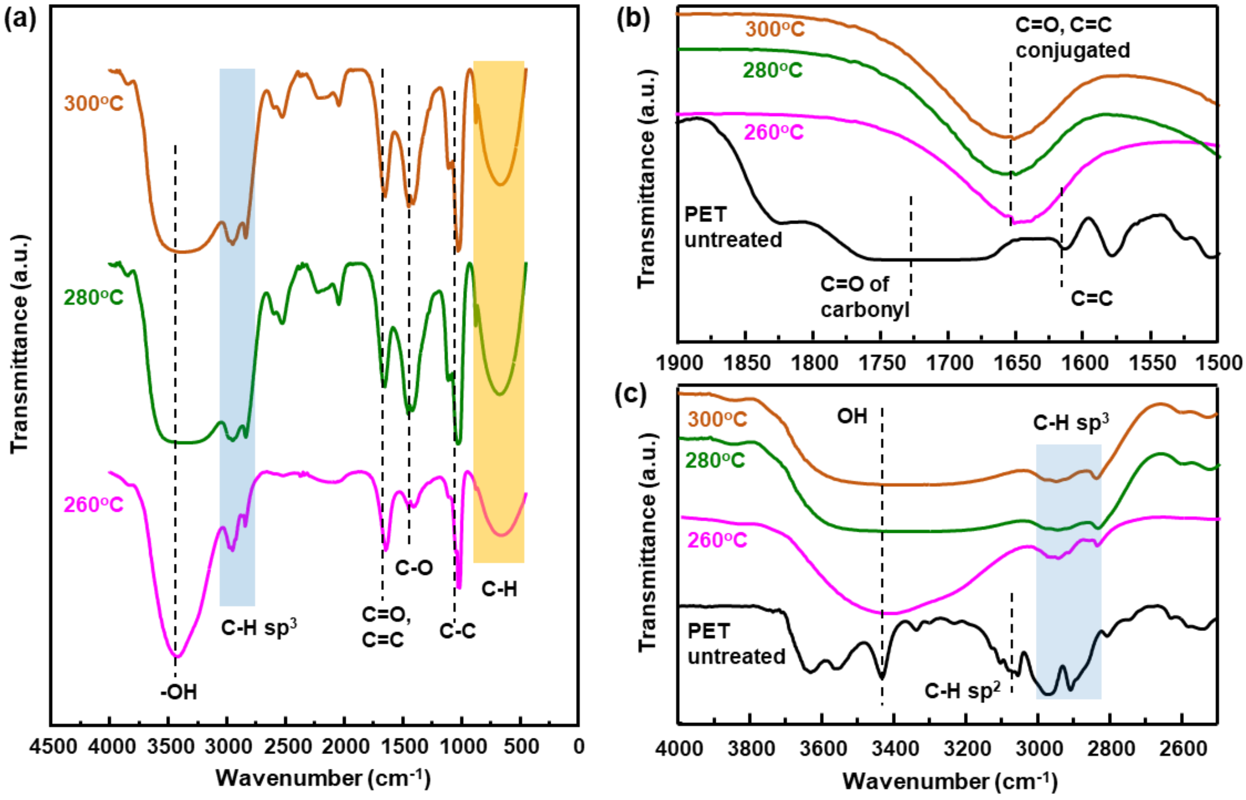


Figure 3. (a) FTIR spectra of PET-CPDs with different temperature heating at full region, (b) FTIR spectra at C=C and C=O region of PET-CPDs with different temperature heating compared with untreated PET, and (c) FTIR spectra at OH, C-H sp^2 and C-H sp^3 region of PET-CPDs with different temperature heating compared with untreated PET.

The morphology and size distribution of PET-based CPDs obtained under optimal conditions were explored by TEM. As displayed in Fig. 4a, PET-based CPDs s are spherical in shape, uniform, and well distributed without aggregation. The particle size distribution histogram represented in the inset of Fig. 2b disclosed their homogeneous size distribution of 1 – 6 nm and average diameter of 3.28 ± 0.74 nm. The structural characteristics of the PET-CPDs were further analyzed using Raman scattering, as shown in Fig 4a. The PET-based CPDs at 260 °C exhibit a Raman peak at 1300 cm^{-1}, corresponding to the vibration of aromatic in-plane CH deformation (Xu et al., 2020). There were also peaks at 1620 and 1760 cm^{-1}, attributed to the ring C-C stretching and C=O stretching, respectively (Aoyama et al., 2014). A peak at ~1300 cm^{-1} is often referred to as a peak from the out-of-plane vibrations of sp^2 carbon atoms in the presence of disordered states corresponding to topological sp^3 molecular defect states, while the peak at ~1620 cm^{-1} results from the in-plane stretching vibrations of sp^2 carbon atoms within aromatic domain (Bhattacharyya et al., 2017). However, at higher temperatures (300 °C), the spectral peak broadened, indicating that the structure of CPDs became amorphous. This result implies, based on the emission spectra, that the structure of the CPDs also affects the intensity of the generated emissions. Crystalline structures are expected to emit more optimally than amorphous structures due to reduced phonon (non-radiative) scattering losses (Pal et al., 2018).

The XRD pattern of the synthesized PET-based CPDs is shown in Fig 4c. For comparison, the XRD pattern of untreated PET was also recorded. The XRD of the PET before and after treatment show a noticeable change. The raw PET shows the characteristic peak at $2\theta = 25.5^o$ corresponding to the (100) plane for a semicrystalline PET. After heat treatment, there is also new peaks at 17.5° and 22.5° corresponding to the (110) and (010) planes, respectively. The observed peak at a 2θ of 22.5° can be attributed to the increased presence of the amorphous region in contrast to the crystalline region (Agrawal et al., 2018). This observation implies that the heating treatment has an impact on the surface of PET.

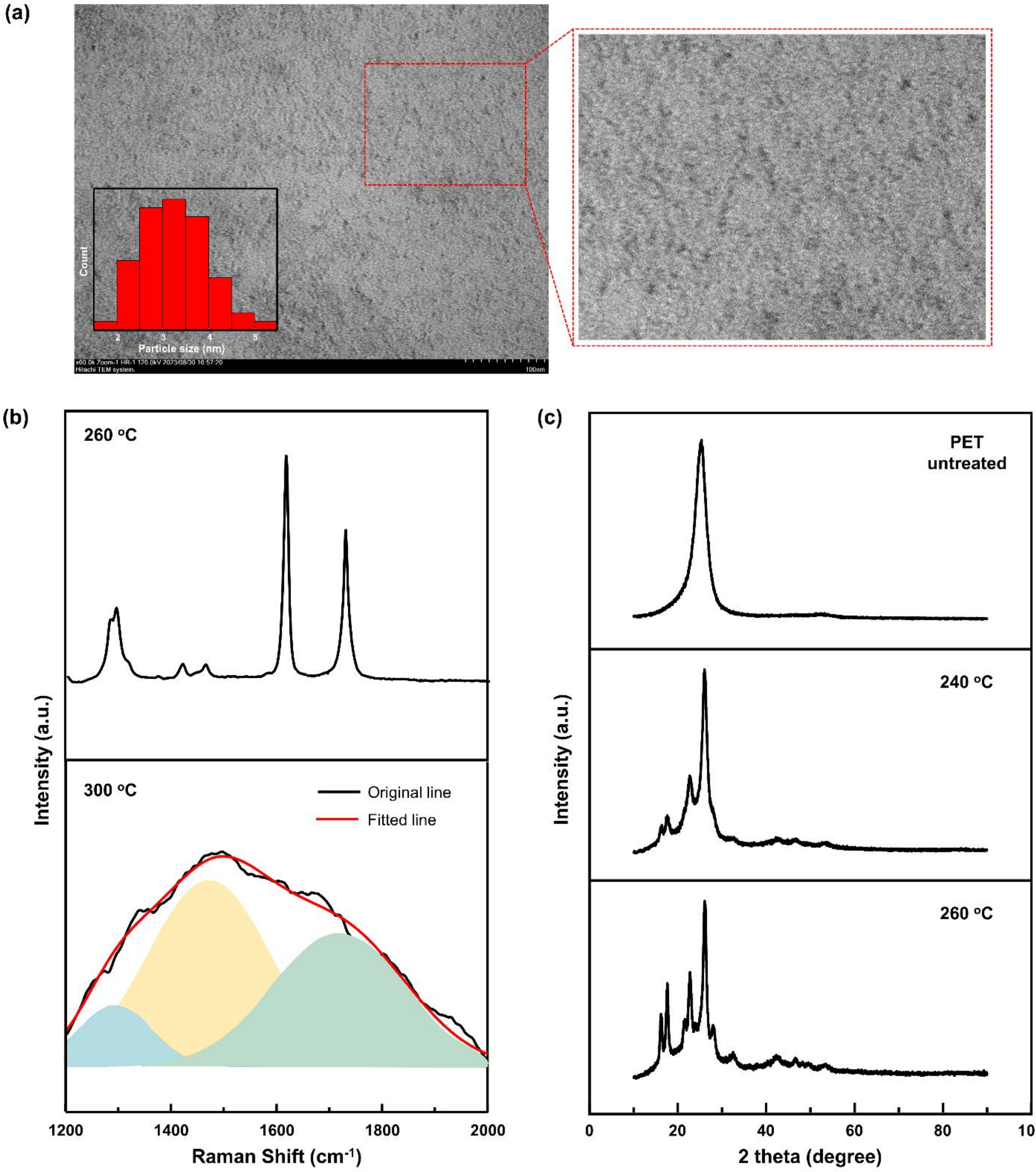


Figure 4. (a) TEM of PET-CPDs by heating at 260 ^{o}C (b) Raman shifts of PET-CPDs by heating at 260 ^{o}C and 300 ^{o}C, and (c) XRD of PET and PET-CPDs by heating at 240 ^{o}C and 260 ^{o}C

The role of reaction time on the properties of the materials is displayed in Fig 5. Again, the emission of the PET-based CPDs strongly depends on the reaction time as well. The physical appearance of PET-based CPDs (Fig. 5a) indicates that the sample is photoluminescent after being heated for more than 1 hour at a heating temperature over the melting point (260 ^{o}C). Optimal emission is observed in PET-based CPDs heated for 2.5 hours, as demonstrated by the photoluminescence spectra shown in Fig. 5b. Modifying the heating time results in a shift in the emission peak of the PET-based CPDs to 450 nm, similar to the variation observed with heating temperature. As illustrated in Fig 5c, the highest intensity of the PET-based CPDs was observed at 2.5 hours of heating, followed by a decrease in intensity after heating for 3 hours.

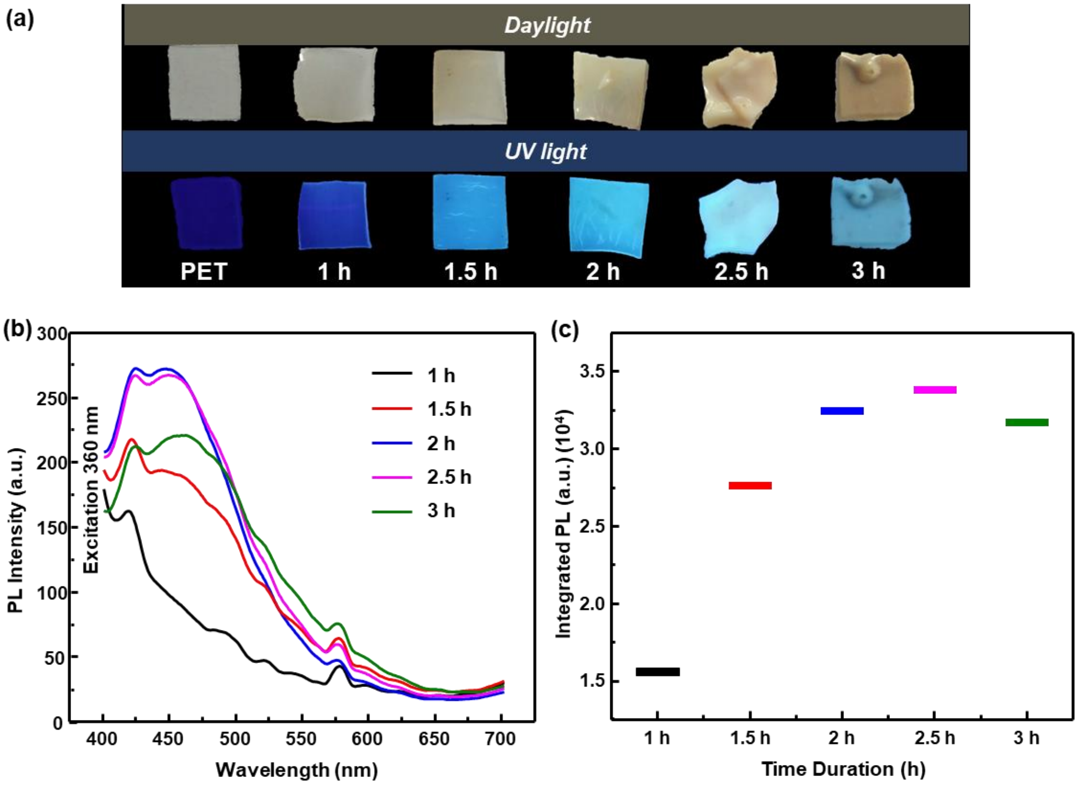


Figure 5. Dependence of the photoluminescence (PL) properties of CPDs on heating time: a) physical appearance emission of PET-CPDs, (b) PL spectra of PET-CPDs, and (c) integrated PL as a function of time duration of hearing and PL intensity.

Fig 6 summarizes our findings. The schematic correlates the PL intensity of the PET-CPDs obtained during different stages of heating, which is primarily attributed to the conjugation of the aromatic core. As the temperature increases, the number of oxygen-containing groups grows and contributes to the suppressed emission of the aromatic core. The optimal PL intensity is observed in PET-based CPDs at 260 ^{o}C with a 2.5 h heating duration. Initially, the polymer of PET is non-fluorescent molecules. However, under low heating temperatures (below its melting point), the PET bonds do not decompose but become more wrinkled. When the degree of heating is increased above the melting point (260 ^{o}C), the PET carbon chain linkages decompose and carbonize, forming carbon core CPDs with a conjugated aromatic core structure. This conjugation determines the photoluminescence properties of the CPDs. At higher temperatures (from 280 ^{o}C to 300 ^{o}C), the carbon core gradually grows, and the number of oxygen-containing groups on the surface of PET-based CPDs increases, leading to a decrease in the intensity of CPDs. The duration of heating also has a significant impact on the intensity of PET-based CPDs obtained. The carbon chain bonds decompose by heating PET above its melting point (260 ^{o}C), but sufficient heating time is necessary to generate an appropriate carbon core with conjugated bonds. In this study, the optimal duration was 2.5 hours. In conclusion, the PL intensity of PET-based CPDs is influenced by the number of oxygen-containing groups and the growth of the carbon core so that the PET-based CPDs with the highest intensity PL is obtained at appropriate heating temperature and duration.

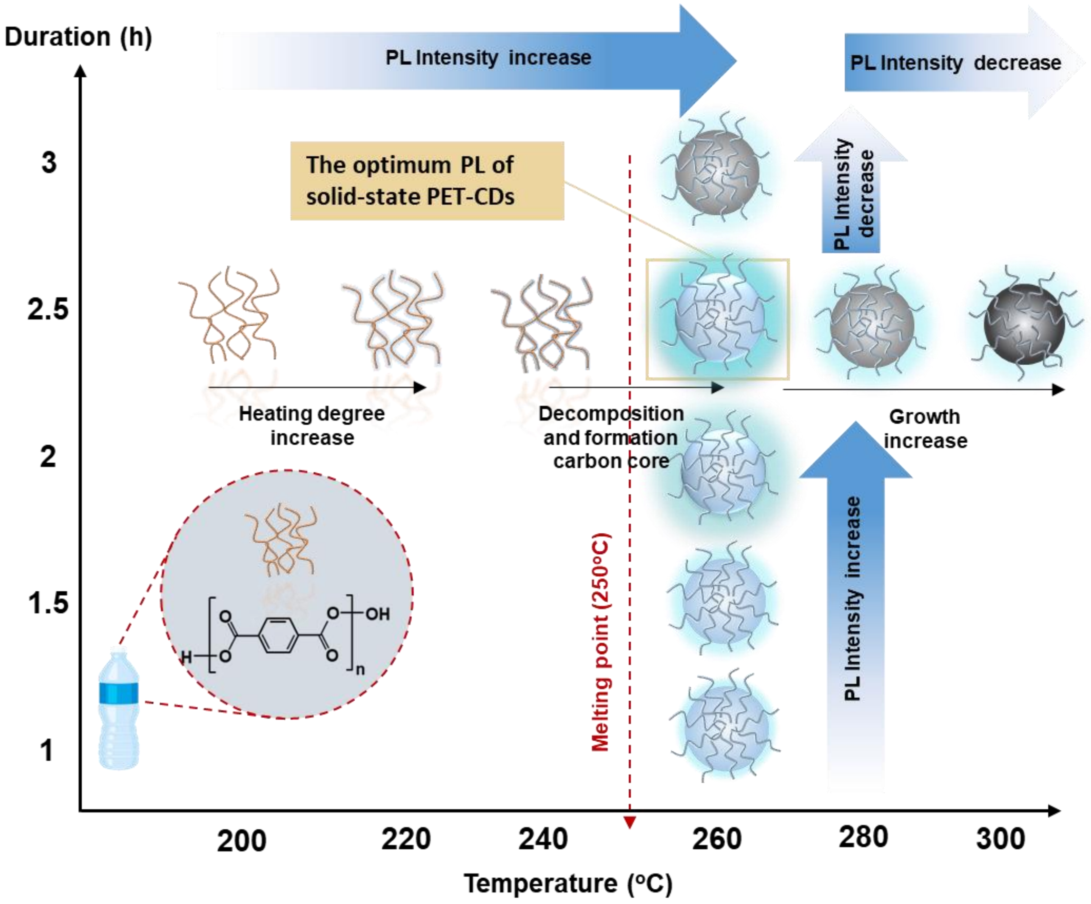


Fig 6. Schematic representation of the emission characteristics of PET-CPDs over temperature and time scales and schematic possibility of mechanism of CPDs formation.

In comparison to CPDs material derived from PET that has been previously reported, our CPDs exhibit comparable results to most reports (Table 1). It is worth mentioning that some reports showed a more complicated and expensive synthesis process, suggesting our PET-CPDs provide better economic value. Additionally, the mass product yield of the PET-CPDs in a single manufacturing process is 0.028 grams. Due to the relatively low temperature employed (slightly higher than the melting point and significantly lower than the weight loss temperature), the utilized method has great potential for large-scale production of CPDs.

Table 1. Comparison of various reported CPDs material from PET

No	Synthetic method	Reaction condition	Product	Average size	Emission	Ref.
1.	Microwave reactor – hydrothermal method	260 ^oC, 24 h	Solution	2.8 nm	Green	(Wu et al., 2022)
2.	Two-step approach (carbonization followed by hydrothermal treatment)	muffle furnace at 350 ^oC for 2 h, autoclave at 170 ^oC for 8 h	Solution	6 nm	Blue	(Ghosh and Das, 2021)
3.	Heating – hydrothermal method	Heated at 350 °C for 2 h, Hydrothermal 180 ^oC for 12 h	Solution	6 nm	Blue	(Hu et al., 2019)
4.	Air oxidation	300 ^oC for 2 h then immerse in H_2SO_4 at 120^oC for 6 h	Solution	3 nm	-	(Hu et al., 2021)
5.	Quenched into liquid nitrogen	-	Yellowish paste	2.3 nm	Blue	(Yin et al., 2021)
6.	Heating treatment	260^oC, 2 h	Solid	3.27 nm	Blue	This work

4. Conclusions

In summary, we have demonstrated a one-step synthetic route to convert PET bottle waste into solid-state fluorescent CPDs. The PL properties of the solid-state PET-CPDs prepared by a heating method strongly depend on the temperature and duration. This study used the thermal decomposition (melting point) of PET to determine the synthesis temperature and could study the effect of that temperature on the PL properties of PET-based CPDs. We discovered that

PET-based CPDs fabricated at 260 °C for 2.5 hours exhibit the highest fluorescence intensity. The results indicate that the melting point of PET plays a crucial role the in formation of conjugation aromatic core of CPDs. The carbonization degree would increase not only at longer heating durations, but also as a result of higher heating temperatures after melting point. These findings offer a promising solution for plastic waste management and a simple, green synthesis route for the production of solid-state fluorescent CPDs without the problem of self-quenching.

5. Author Contributions

Mahardika Prasetya Aji: original idea, conceptualization, supervision, and writing-review & editing. Ita Rahmawati: conceptualization, methodology, investigation, writing-original draft, and writing-review & editing. Aan Priyanto: writing-review & editing and visualization. Putut Marwoto: supervision and visualization.

6. Conflict of interest

There are no conflicts to declare.

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Novel one-step synthesis of solid-state carbonized polymer dots by heating at around melting point of polyethylene terephthalate (PET) bottle plastic waste

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Abstract

Production of luminescent carbonized polymer dots (CPDs) in the solid state has been a crucial challenge due to their tendency to self-aggregate, leading to fluorescence quenching and limiting their applicability in the solid state. In this work, we present an environmentally friendly method for producing solid-state CPDs with high photoluminescence (PL) intensity by simple one-step heating method using waste PET bottle plastic as the raw material. Based on the PET thermal analysis, heating temperatures between 200 °C and 300 °C and heating duration were explored. Through systematic experimentation, we discovered that heating temperature and time play a crucial role in controlling PL intensity, ultraviolet-visible (UV-Vis) absorption, carbonization degree, and structure of CPDs. The carbonization of CPDs occurs when the heating temperature exceeds the PET melting point, resulting in strong PL characteristics in the range of 400 and 600 nm. However, when the temperature rises, the PL decreases as the number of oxygen-containing functional groups on the surface of CPDs increases. The optimal conditions for high PL intensity were 260 °C for 2.5 hours. Our one-step heating approach provides a cost-effective solution for recycling PET waste, offering promising potential for various applications.

Keywords: carbonized polymer dots, solid-state fluorescence, polyethylene terephthalate, melting point

1. Introduction

Plastic bottles are commonly encountered packaging materials due to their versatility, durability, and low cost (Benyathiar et al., 2022; Rodríguez-Hernández et al., 2019). It is expected that around 62% of all plastic bottles have been made from polyethylene terephthalate (PET) (Amirudin et al., 2022; Becerril-Arreola and Bucklin, 2021; Zhang et al., 2020). Nowadays, it is very convenient to use PET bottles as single-use beverage packaging. Consequently, disposable PET bottles accumulate as waste and become a significant environmental concern due to their non-biodegradable properties. The biodegradation of PET waste can take up to 500 years and releases harmful toxins into the water and soil, posing risks to human health and biodiversity (Becerril-Arreola and Bucklin, 2021; Gao et al., 2022; Ghosh and Das, 2021). Incineration is a common method for disposing of PET waste, but it contributes to air pollution and releases high CO_2 emissions that exacerbate greenhouse effects and climate change (Song et al., 2019; Yin et al., 2021). Thus, there is a pressing need for a more environmentally friendly method to increase the value of these waste materials. Recently, alternative methods have been developed to process PET wastes as a promising source for synthesis of carbon-based nanomaterial, such as carbon dots (Ghosh and Das, 2021; Hu et al., 2021, 2019; Johnson et al., 2021; Rodríguez-Hernández et al., 2019).

Carbonized polymer dots (CPDS) belong to the class of carbon dots and have emerged as a very promising group of zero-dimensional carbon-based nanomaterial that have gained significant attention for their outstanding properties, such as chemical stability, low toxicity, and good optical stability, showing promising potential for many advanced applications (Bagheri et al., 2017; Mansuriya and Altintas, 2021; Song et al., 2019). CPDs have a carbon/polymer hybrid structure with a carbon core, abundant surface functional groups and short polymer chains, which are reserved owing to a low or incomplete carbonization degree (Wang et al., 2021; Xia et al., 2019a). Their characteristics and states can be tunable depending on their application (Mansuriya and Altintas, 2021). In recent years, there has been an increased demand for solid-state CPDs in optoelectronic devices, sensors, fingerprint identification, fluorescent ink, security label, and others (Jin et al., 2020; Singaravelu et al., 2021; Wang et al., 2020). However, solid-state CPDs always suffer from fluorescent quenching due to direct π-π interactions or excessive fluorescence resonance energy transfer (Ren et al., 2021; Singaravelu et al., 2021; Wang et al., 2020), which seriously limits their application in solid-state emissions. Currently, to obtain solid-state fluorescent CPDs, many efforts have been made usually using two main strategies: (i) the synthesis of fluorescent self-quenching-resistant solid-state CPDs, and (ii) blending CPDs with polymers materials to restrict intermolecular motions (Ren et al., 2021; Singaravelu et al., 2021). The second strategy, however, involves a complicated fabrication process and can reduce the optical performance of CPDs (Yoo et al., 2019). Therefore, there is need for the development of solid-state CPDs that are substantially resistant to self-quenching.

Plastic-based CPDs are a great candidate among the various solid-state CPDs since they naturally have hydrophobic qualities, as highlighted by Yin et al (Song et al., 2019). PET plastic-based CPDs, in particular, may also show potential, given their similar properties. Although the final product is liquid-state carbon dots, several studies of PET-based carbon dots have been performed using a two-step synthesis method. Ghosh and Das reported the heating of PET to high temperatures at the first step of synthesis, producing a dark and dry powder resembling carbon black (Ghosh and Das, 2021). Similarly, Hu et al. also conducted a two-step synthesis with the heating of PET at the first step (Hu et al., 2021). However, if the carbonization temperature is optimized, solid-state CPDs with high fluorescent can be yielded without requiring a second synthesis step. As Bagheri and his coworkers reported, the optimum carbonization degree in the synthesis carbon dots was affected by melting point of starting material during heating process. The photoluminescent behavior of carbon dots strongly depends on the temperature of heating during synthesis (Bagheri et al., 2017). To the best of our knowledge, there have been no reports on the investigation of PET-based CPDs in a solid state. Specifically, synthesis according to the thermal decomposition of PET has not been considered.

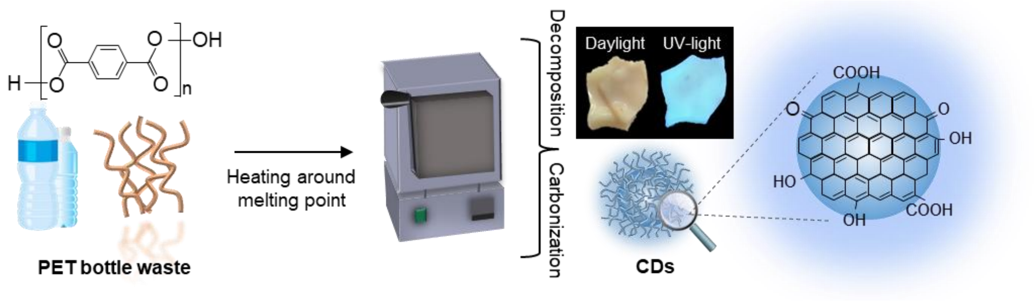
This study reported a simple synthesis route for producing solid-state CPDs from PET plastic waste. An experiment plan was arranged to gather the maximum information possible regarding the formation of these materials and the impact of synthesis conditions on their optical and chemical composition. The heating temperatures were investigated around the melting point of PET because carbon chains in the polymer decompose at temperatures above the melting point, which may lead to nucleation processes generating carbon cores. This study opens up a new understanding of the melting temperature as a critical point for synthesizing CPDs which only a few researchers have pointed out. In addition, the synthesis process does not require toxic, corrosive, or expensive solvents which are typically employed in synthesizing CPDs. The production of solid-state fluorescent CPDs from PET plastic waste increases the added value of PET waste and opens opportunities for future research in plastic waste management.

2. Material and Methods

Synthesis of CPDs. The solid-state CPDs were prepared by a one-step heating method using PET bottle waste as a carbon source. First, a waste PET bottle was collected and washed subsequently using water. The dried PET bottle was cut into small flakes and, afterward, transferred in a crucible for air oxidation in a muffle furnace at various temperatures ranging from 200 ^{o}C to 300 ^{o}C for 2.5 hours. The optimal temperature was determined to be 240 °C and was selected for the heating durations of 1 hour to 3 hours. The resulting solid-state product was collected and then characterized.

Characterization. UV-visible absorption spectra were recorded using a BMG Labtech Fluostar Omega spectrometer. Fluorescence measurements were carried out using a Cary Eclipse MY14440002 spectrofluorometer. Integrated fluorescence intensity is the area under the PL curve in the wavelength range from 400 to 650 nm. Fourier Transform Infrared (FTIR) spectra were recorded for powder CPDs using the Perkin-Elmer Spectrum Version 10.03.06 with an ATR attachment. Thermogravimetric analysis (TGA) was performed using a STA7300 Hitachi with a heating rate of 20 °C/min and 50 ^{o}C/min. Raman spectroscopy was measured using Horiba LabRAM HR Evolution Laser 785 nm. XRD measurements were performed using a Rigaku Smart Lab X-Ray diffractometer with CuKα radiation at a wavelength of $\lambda = 1.540\ \dot{A}$ to determine the crystalline phase of the synthesized samples. The size of the CPDs were investigated using TEM measurements performed on a HT7700 Hitachi at 80 kV.

3. Results and Discussion



Scheme 1. Mechanism for the preparation of solid-state CPDs based on PET bottle waste

The solid-state CPDs were synthesized from PET bottle waste using a simple heating process in a muffle furnace without any additional chemicals (Scheme 1). In preparing CPDs using the heating method, the PET chains were decomposed, followed by carbonization and then solid-state CPDs were formed. In this study, a systematic synthesis study was conducted by setting the synthesis temperature at around the melting point of PET and varying the heating duration to get the maximum information possible. The DTA of PET bottle waste (Fig. 1a) showed a strong endothermic peak at around 250 °C, implying a melting point of PET. Melting occurs when atomic vibrations are vigorous enough to rupture large numbers of atomic bonds in PET. For polymers, upon cooling through the melting temperature, nuclei form wherein small regions of the tangled and random molecules become ordered and aligned. At temperatures in excess of the melting temperature, these nuclei are unstable due to the thermal atomic vibrations that tend to disrupt the ordered molecular arrangements. After nucleation and during the growth stage, nuclei grow through the continued ordering and alignment of additional molecular chain segments (Callister, 2001). On the other hand, the TGA curve (Fig 1b and c) confirmed a decrease in weight loss, with the thermal degradation of PET onsets at 380 ^{o}C (at heating rate 20 ^{o}C/min) and at 395 ^{o}C (at heating rate 50 ^{o}C/min). The results also reveal that the heating rate affects the DTA and TGA test results, however the difference is not significant.

Furthermore, FTIR analysis shows that PET plastic bottles (Fig. 2d) showed the presence of broad molecular groups consisting of carbon, hydrogen, and oxygen. The C-H stretching vibration modes appear in the region 3000-2825 cm^{-1} that refer to the functional groups such as alkyl, alkanal, alkyne, alkene, and arene. The C-H bending mode of vibration, which has weaker bond strength than their stretching modes, appears in the region 924-808 cm^{-1} and 573 cm^{-1} (Prasad et al., 2011). The absorption at 3412 cm^{-1} is assigned to the O-H stretching at the end group of the PET molecule chain. The C=O stretching and the aromatic skeleton stretching bands were observed at 1730 and 1614 cm^{-1}, respectively (Torres-Huerta et al., 2016).

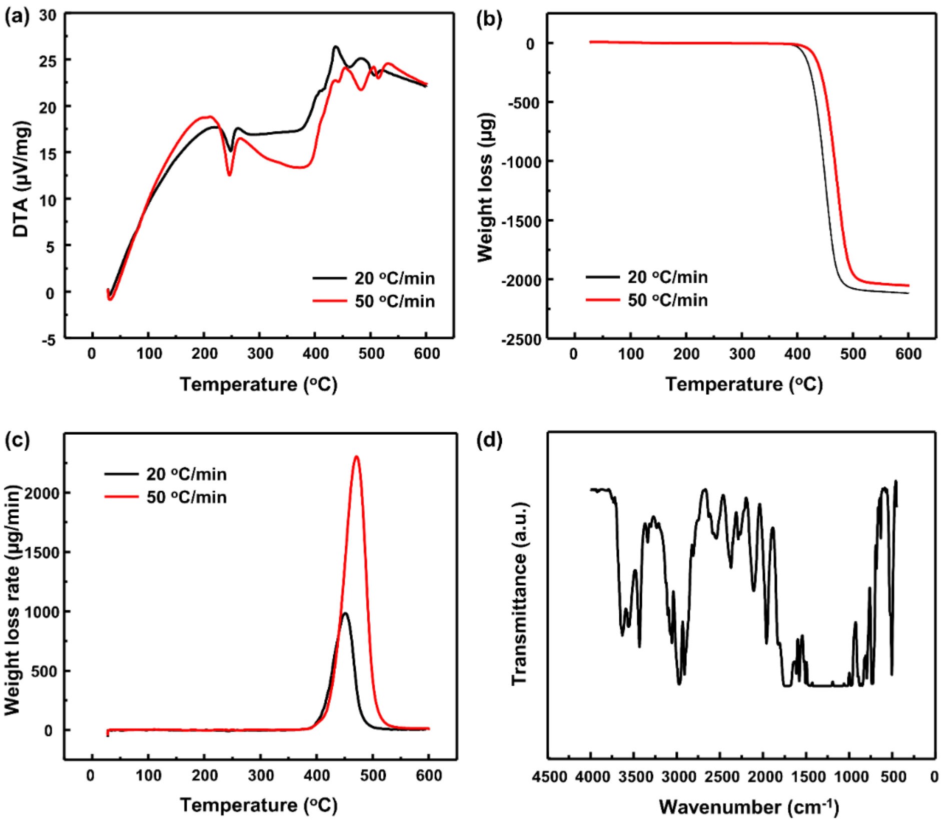


Figure 1. Starting material (PET bottle waste) analysis: (a) differential thermal analysis (DTA), (b) thermogravimetric analysis (TGA), (c) derivative TGA (DTGA), and (d) Fourier Transform Infrared Spectroscopy (FTIR).

The distribution of the samples with different heating temperatures is shown in Fig 2a. Physically, the samples heated at temperatures ranging from 200 to 240 ^{o}C (below the melting point) remained transparent but exhibited increased brittleness and shrinkage compared to the unheated sample. On the other hand, the samples heated over the melting point (260-300 ^{o}C) showed significant physical alteration, such as becoming opaque, extremely brittle, and undergoing a color from light brown to dark brown. Moreover, under UV light, the results revealed that samples heated between 200-240 ^{o}C exhibited no luminescence. Meanwhile, samples of 260-300 ^{o}C showed luminescence, with samples of 260 ^{o}C having the brightest luminescence. This result indicated that determining the synthesis temperature around the melting point is one of the most crucial variables in producing CPDs with excellent luminescence.

The UV-Vis absorption spectra of the samples with varying synthesis temperatures are depicted in Fig 2b. Samples at 200-240 ^{o}C were not characterized due to their high stickiness and very weak luminescence. The UV-Vis spectra displayed absorption in the UV region of 220-300 nm. A stronger peak was observed at 240 nm with a shoulder at 280 nm originating from π-π* transition of C-C and C=C in aromatic rings of the carbon core and n-π* transition of oxygen-related bonds (C=O and C-O) on the surface state of CPDs, respectively (Ding et al., 2016; Y. Y. Liu et al., 2021). In the case of the 260 °C sample (CPDs-260), the peak at 240 nm was higher than in the other CPDs, indicating that it has stronger absorption properties. This result supports the conclusion that the synthesis temperature has a significant effect on the absorption properties of the synthesized CPDs (Zhang et al., 2016).

The PL spectra of the as-synthesized CPDs at different temperatures are depicted in Fig 2c. Upon excitation at 360 nm, PL intensity also shows a similar trend as the 240 nm peak of CPDs absorption intensity, suggesting the luminescence of solid-state PET-based CPDs may originate from the π-π* bond transition in the carbon core. Widely proposed luminescence mechanisms of CPDs originate from the conjugated π-domain within the graphitic carbon core, the surface state, or the molecular state of CPDs (Ai et al., 2021; Xia et al., 2019b). Here, the emission of PET-based CPDs belonged to the core-state luminescence mechanism category. Under 360 nm irradiation, the luminescence of solid-state CPDs centered at 450 nm, indicating blue color (in line with the physical appearance Fig. 2a). Additionally, it is apparent that the photoluminescence (PL) spectrum has a little peak at a wavelength of 575 nm. The observed peak suggests that PET-CPDs exhibit multiple emission centers, with the additional emission usually due to the presence of polycyclic aromatic hydrocarbons of varying sizes. This is in comparison with the conjugated sp^2 domains formed during the dehydration of the polymeric structure (Shamsipur et al., 2018).

As shown in Figure 2d, the integrated fluorescence intensity is derived from the area under the PL curve in the 400 to 650 nm range. The PL intensity changes with heating temperature, and CPDs-260 has the highest intensity. However, the PET-based CPDs emit less light and look black when the heating temperature is quite higher than the melting point, indicating that carbonization occurs during the formation of CPDs. Due to the severe aggregation-caused quenching, most CPDs show no fluorescence in the solid state (B. Liu et al., 2021). This study obtained solid-state PET-CPDs with strong blue photoluminescence without aggregation. The observed phenomenon can be attributed to the presence of a large number of surface PET chains surrounding the core of CPDs, which effectively prevents π-π interactions. Consequently, the quenching process induced by aggregation is blocked. In addition, it is worth noting that PET-CPDs exhibit strong hydrophobic characteristics, in contrast to many other CPDs that possess hydrophilic surfaces. This characteristic limits the electrostatic interaction and particle attraction of CPDs (Ru et al., 2022; Yang et al., 2019).

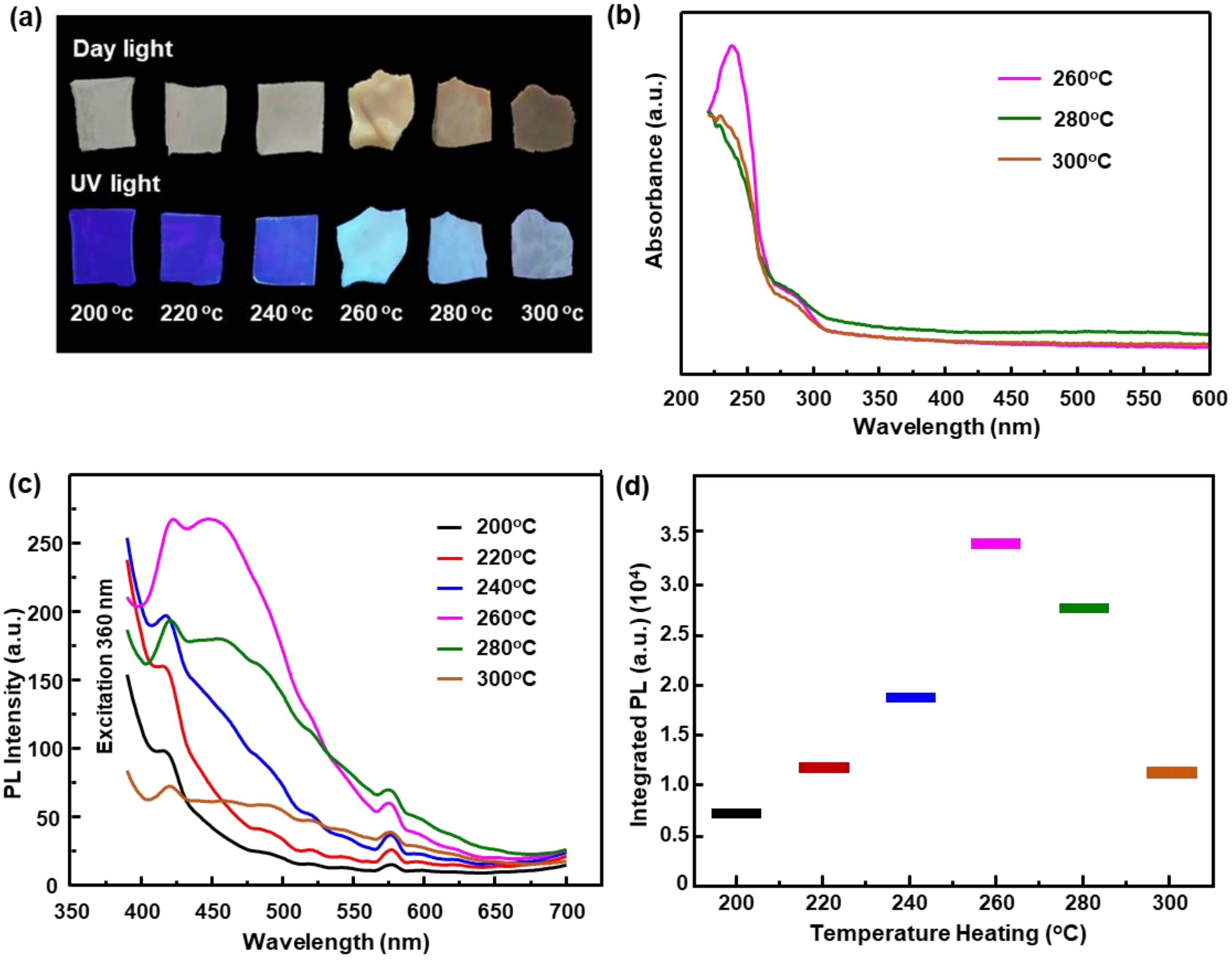


Figure 2. (a) Solid-state PET-based CPDs under visible light (up) and UV radiation (down) over heating temperature variation, (b) UV-Vis absorption of solid-state PET-based CPDs, (c) PL

spectra of the solid-state PET-based CPDs samples under 360 nm, (d) integrated PL of spectra PL from 400 to 650 nm wavelength.

As shown in Fig. 3, Fourier Transform Infrared (FTIR) was performed to determine the composition of the PET-CPDs. The FTIR results confirmed the presence of different functional groups in the synthesized CPDs, including oxygen, hydrogen, and carbon (Fig. 3a). Compared to the FTIR results of untreated PET, some of the PET composition significantly changed after heating above the melting point, indicating decomposition occurred during the heating process (Fig 3a). The absorbance at 1430 cm^{-1} changed significantly, indicating a C-O group presence. The higher the temperature, the more energy the sample will attach to ambient oxygen. In addition, changes at 1670 cm^{-1} were observed, indicating conjugated C=C and C=O bonds (Fig. 3b). The untreated PET showed a C=C bond from the aromatic skeleton at 1610 cm^{-1} and the C=O bond from the carbonyl at 1720 cm^{-1}. However, when the PET was heated above the melting point, the C=C and C=O frequencies shifted and were no longer distinguishable, moving to 1660 cm^{-1} and indicating conjugation of the carbonyl group with a C=C double bond. The presence of the C=C and C=O bond signatures suggests forming a π-conjugated system as CPDs core structure (Permatasari et al., 2021). This conjugation bond plays a role in the CPDs photoluminescence process, which is related to the energy gap (Permatasari et al., 2021; Semeniuk et al., 2019; Wang et al., 2017). The results of this study demonstrate that temperatures above the melting point can lead to the formation of conjugate bonds in the aromatic skeleton of the PET-based CPDs, resulting in solid luminescence. However, CPDs-280 and CPDs-300 have lower luminescence intensity (as previously demonstrated in Fig 2c) due to a large number of attached oxygen bonds. These oxygen-containing groups lead to non-radiative coupling of electron-hole pairs that suppress CPDs PL (Ai et al., 2021). In addition, as depicted in Fig. 3c, PET-CPDs feature C-H sp^3 bond vibrations between 3000 to 2800 cm^{-1}, suggesting the carbon core of the PET-CPDs. In contrast, untreated PET possessed C-H sp^2 bonds that vanished upon heating, indicating that heating at temperatures above the melting point decomposed the original PET structure.

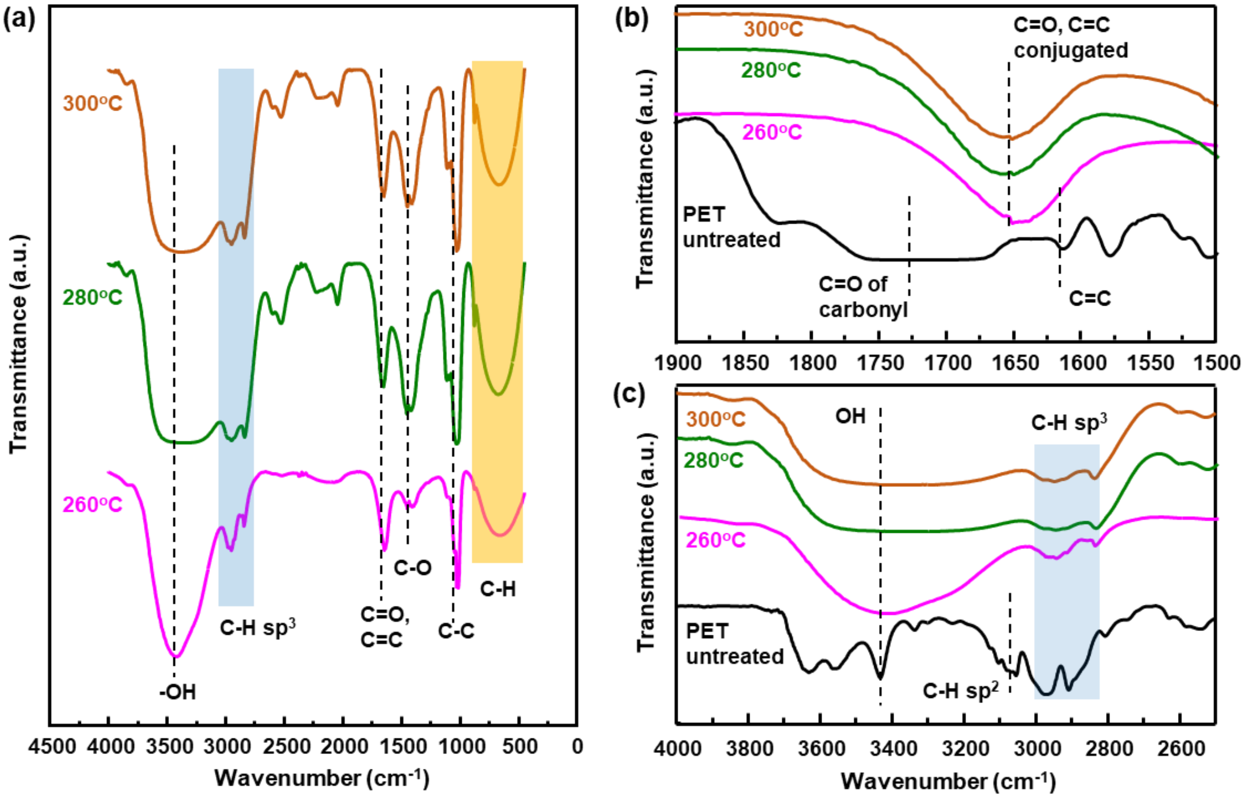


Figure 3. (a) FTIR spectra of PET-CPDs with different temperature heating at full region, (b) FTIR spectra at C=C and C=O region of PET-CPDs with different temperature heating compared with untreated PET, and (c) FTIR spectra at OH, C-H sp^2 and C-H sp^3 region of PET-CPDs with different temperature heating compared with untreated PET.

The morphology and size distribution of PET-based CPDs obtained under optimal conditions were explored by TEM. As displayed in Fig. 4a, PET-based CPDs s are spherical in shape, uniform, and well distributed without aggregation. The particle size distribution histogram represented in the inset of Fig. 2b disclosed their homogeneous size distribution of 1 – 6 nm and average diameter of 3.28 ± 0.74 nm. The structural characteristics of the PET-CPDs were further analyzed using Raman scattering, as shown in Fig 4a. The PET-based CPDs at 260 °C exhibit a Raman peak at 1300 cm^{-1}, corresponding to the vibration of aromatic in-plane CH deformation (Xu et al., 2020). There were also peaks at 1620 and 1760 cm^{-1}, attributed to the ring C-C stretching and C=O stretching, respectively (Aoyama et al., 2014). A peak at ~1300 cm^{-1} is often referred to as a peak from the out-of-plane vibrations of sp^2 carbon atoms in the presence of disordered states corresponding to topological sp^3 molecular defect states, while the peak at ~1620 cm^{-1} results from the in-plane stretching vibrations of sp^2 carbon atoms within aromatic domain (Bhattacharyya et al., 2017). However, at higher temperatures (300 °C), the spectral peak broadened, indicating that the structure of CPDs became amorphous. This result implies, based on the emission spectra, that the structure of the CPDs also affects the intensity of the generated emissions. Crystalline structures are expected to emit more optimally than amorphous structures due to reduced phonon (non-radiative) scattering losses (Pal et al., 2018).

The XRD pattern of the synthesized PET-based CPDs is shown in Fig 4c. For comparison, the XRD pattern of untreated PET was also recorded. The XRD of the PET before and after treatment show a noticeable change. The raw PET shows the characteristic peak at $2\theta = 25.5^o$ corresponding to the (100) plane for a semicrystalline PET. After heat treatment, there is also new peaks at 17.5° and 22.5° corresponding to the (110) and (010) planes, respectively. The observed peak at a 2θ of 22.5° can be attributed to the increased presence of the amorphous region in contrast to the crystalline region (Agrawal et al., 2018). This observation implies that the heating treatment has an impact on the surface of PET.

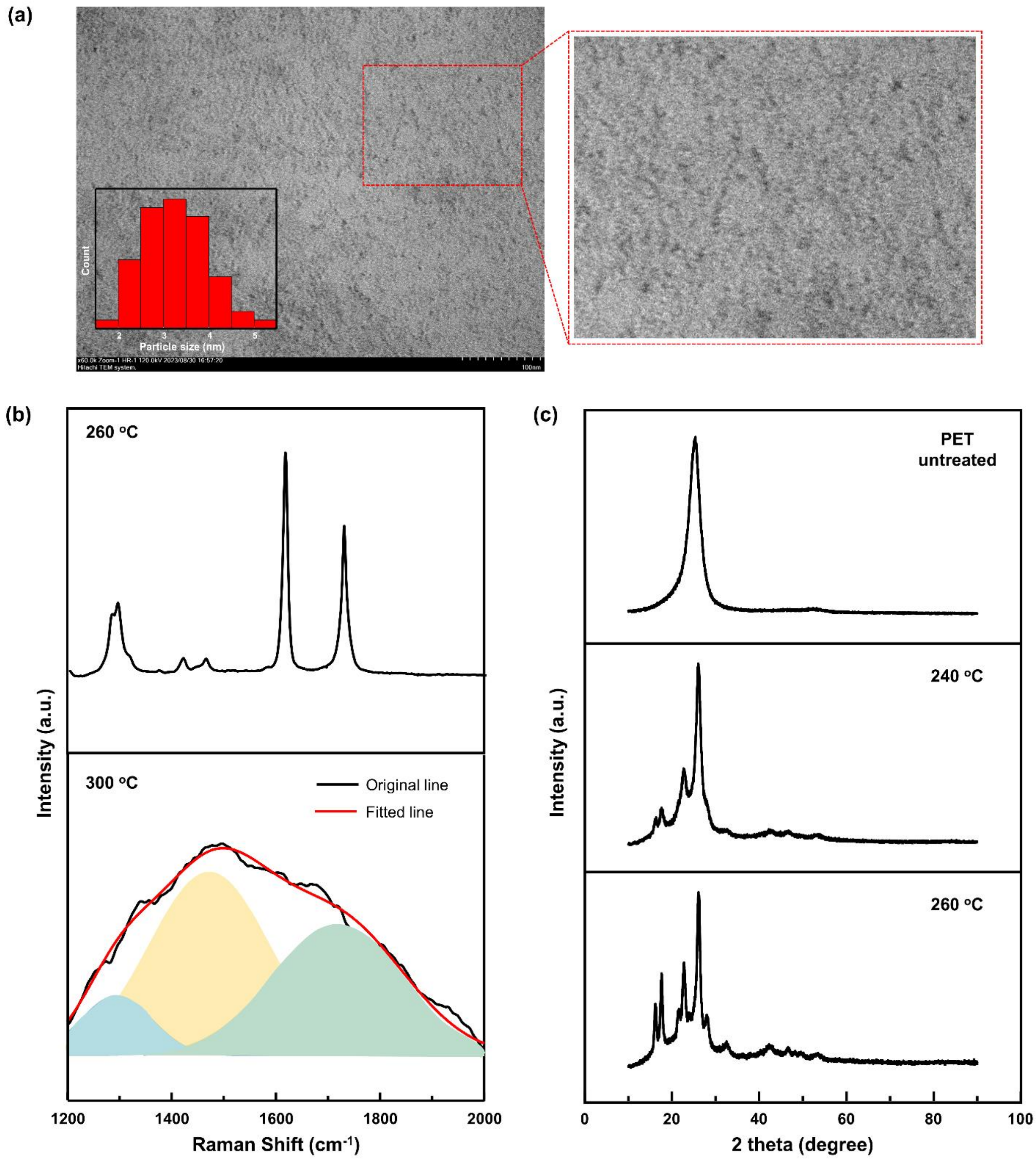


Figure 4. (a) TEM of PET-CPDs by heating at 260 ^{o}C (b) Raman shifts of PET-CPDs by heating at 260 ^{o}C and 300 ^{o}C, and (c) XRD of PET and PET-CPDs by heating at 240 ^{o}C and 260 ^{o}C

The role of reaction time on the properties of the materials is displayed in Fig 5. Again, the emission of the PET-based CPDs strongly depends on the reaction time as well. The physical appearance of PET-based CPDs (Fig. 5a) indicates that the sample is photoluminescent after being heated for more than 1 hour at a heating temperature over the melting point (260 ^{o}C). Optimal emission is observed in PET-based CPDs heated for 2.5 hours, as demonstrated by the photoluminescence spectra shown in Fig. 5b. Modifying the heating time results in a shift in the emission peak of the PET-based CPDs to 450 nm, similar to the variation observed with heating temperature. As illustrated in Fig 5c, the highest intensity of the PET-based CPDs was observed at 2.5 hours of heating, followed by a decrease in intensity after heating for 3 hours.

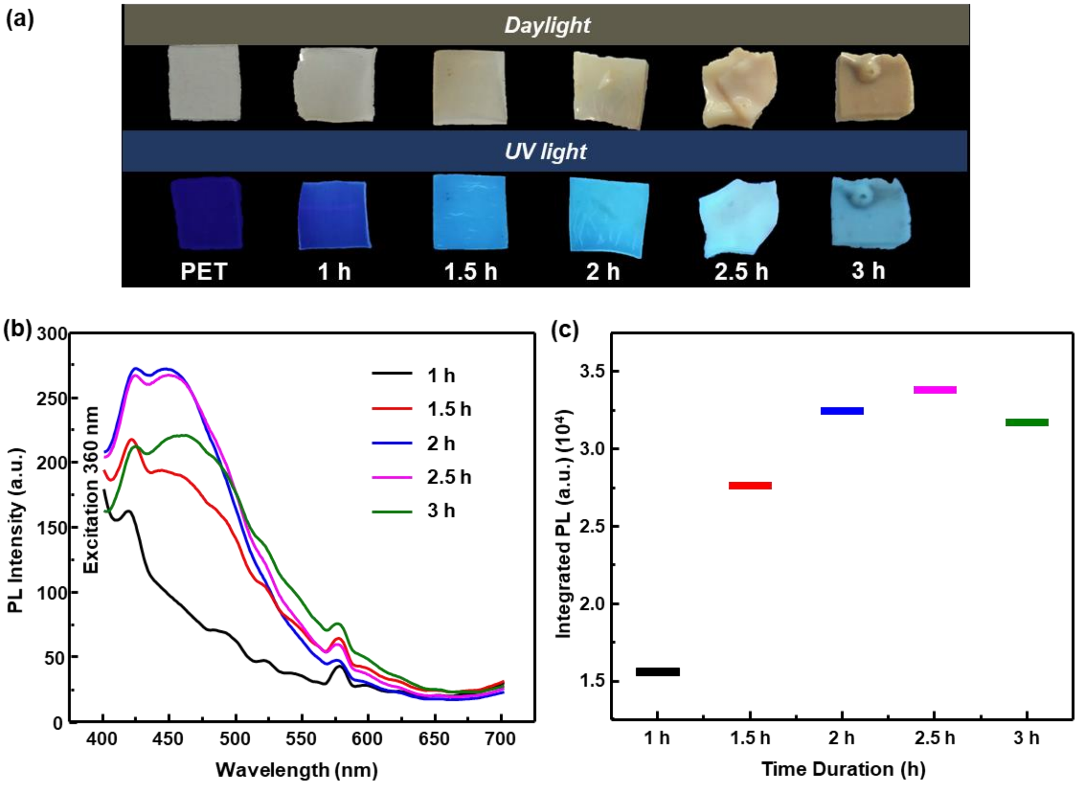


Figure 5. Dependence of the photoluminescence (PL) properties of CPDs on heating time: a) physical appearance emission of PET-CPDs, (b) PL spectra of PET-CPDs, and (c) integrated PL as a function of time duration of hearing and PL intensity.

Fig 6 summarizes our findings. The schematic correlates the PL intensity of the PET-CPDs obtained during different stages of heating, which is primarily attributed to the conjugation of the aromatic core. As the temperature increases, the number of oxygen-containing groups grows and contributes to the suppressed emission of the aromatic core. The optimal PL intensity is observed in PET-based CPDs at 260 °C with a 2.5 h heating duration. Initially, the polymer of PET is non-fluorescent molecules. However, under low heating temperatures (below its melting point), the PET bonds do not decompose but become more wrinkled. When the degree of heating is increased above the melting point (260 °C), the PET carbon chain linkages decompose and carbonize, forming carbon core CPDs with a conjugated aromatic core structure. This conjugation determines the photoluminescence properties of the CPDs. At higher temperatures (from 280 °C to 300 °C), the carbon core gradually grows, and the number of oxygen-containing groups on the surface of PET-based CPDs increases, leading to a decrease in the intensity of CPDs. The duration of heating also has a significant impact on the intensity of PET-based CPDs obtained. The carbon chain bonds decompose by heating PET above its melting point (260 °C), but sufficient heating time is necessary to generate an appropriate carbon core with conjugated bonds. In this study, the optimal duration was 2.5 hours. In conclusion, the PL intensity of PET-based CPDs is influenced by the number of oxygen-containing groups and the growth of the carbon core so that the PET-based CPDs with the highest intensity PL is obtained at appropriate heating temperature and duration.

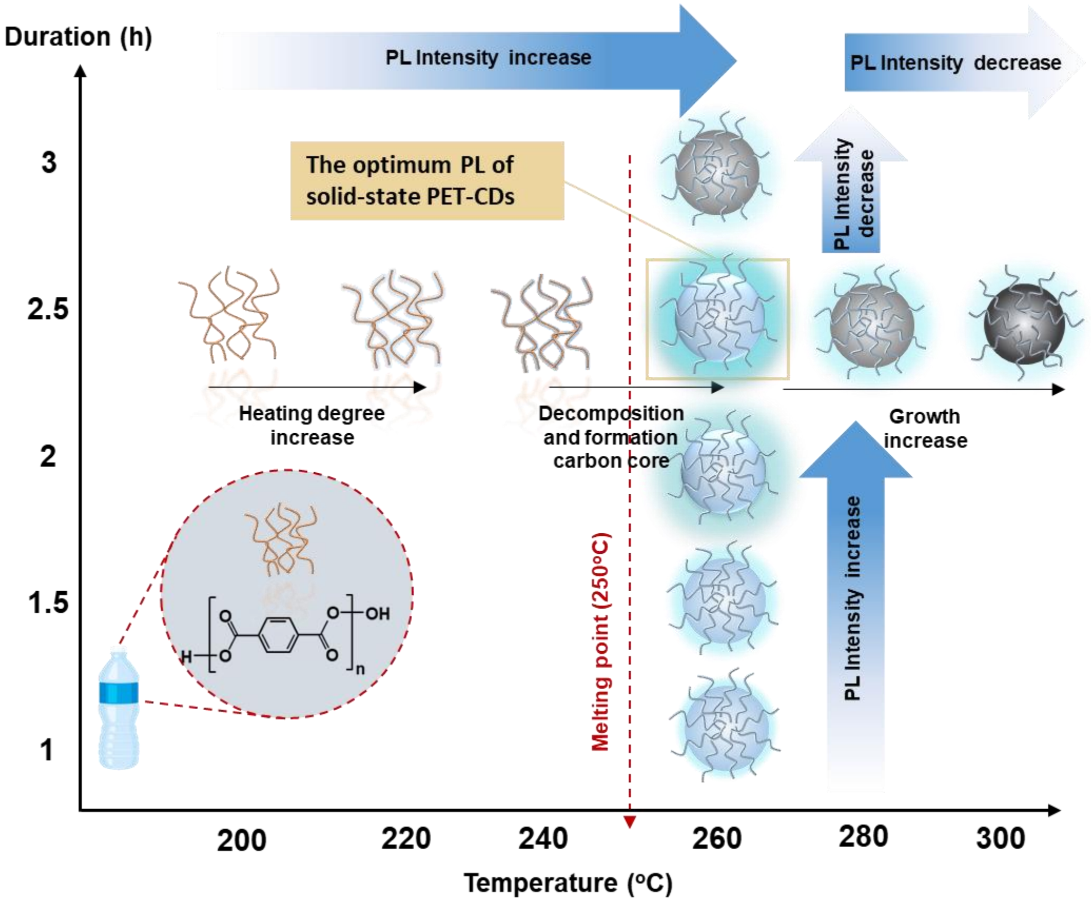


Fig 6. Schematic representation of the emission characteristics of PET-CPDs over temperature and time scales and schematic possibility of mechanism of CPDs formation.

In comparison to CPDs material derived from PET that has been previously reported, our CPDs exhibit comparable results to most reports (Table 1). It is worth mentioning that some reports showed a more complicated and expensive synthesis process, suggesting our PET-CPDs provide better economic value. Additionally, the mass product yield of the PET-CPDs in a single manufacturing process is 0.028 grams. Due to the relatively low temperature employed (slightly higher than the melting point and significantly lower than the weight loss temperature), the utilized method has great potential for large-scale production of CPDs.

Table 1. Comparison of various reported CPDs material from PET

No	Synthetic method	Reaction condition	Product	Average size	Emission	Ref.
1.	Microwave reactor – hydrothermal method	260 ^{o}C, 24 h	Solution	2.8 nm	Green	(Wu et al., 2022)
2.	Two-step approach (carbonization followed by hydrothermal treatment)	muffle furnace at 350 ^{o}C for 2 h, autoclave at 170 ^{o}C for 8 h	Solution	6 nm	Blue	(Ghosh and Das, 2021)
3.	Heating – hydrothermal method	Heated at 350 °C for 2 h, Hydrothermal 180 ^{o}C for 12 h	Solution	6 nm	Blue	(Hu et al., 2019)
4.	Air oxidation	300 ^{o}C for 2 h then immerse in H_2SO_4 at 120^{o}C for 6 h	Solution	3 nm	-	(Hu et al., 2021)
5.	Quenched into liquid nitrogen	-	Yellowish paste	2.3 nm	Blue	(Yin et al., 2021)
6.	Heating treatment	260^{o}C, 2 h	Solid	3.27 nm	Blue	This work

4. Conclusions

In summary, we have demonstrated a one-step synthetic route to convert PET bottle waste into solid-state fluorescent CPDs. The PL properties of the solid-state PET-CPDs prepared by a heating method strongly depend on the temperature and duration. This study used the thermal decomposition (melting point) of PET to determine the synthesis temperature and could study the effect of that temperature on the PL properties of PET-based CPDs. We discovered that

PET-based CPDs fabricated at 260 °C for 2.5 hours exhibit the highest fluorescence intensity. The results indicate that the melting point of PET plays a crucial role the in formation of conjugation aromatic core of CPDs. The carbonization degree would increase not only at longer heating durations, but also as a result of higher heating temperatures after melting point. These findings offer a promising solution for plastic waste management and a simple, green synthesis route for the production of solid-state fluorescent CPDs without the problem of self-quenching.

5. Author Contributions

Mahardika Prasetya Aji: original idea, conceptualization, supervision, and writing-review & editing. Ita Rahmawati: conceptualization, methodology, investigation, writing-original draft, and writing-review & editing. Aan Priyanto: writing-review & editing and visualization. Putut Marwoto: supervision and visualization.

6. Conflict of interest

There are no conflicts to declare.

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Mahardika Prasetya Aji: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data Curation, Writing - Original Draft, Supervision. **Ita Rahmawati:** Conceptualization, Methodology, Formal analysis, Investigation, Data Curation, Writing - Review & Editing, Visualization. **Aan Priyanto:** Formal analysis, Investigation, Data Curation, Writing - Review & Editing, Visualization. **Putut Marwoto:** Conceptualization, Validation, Formal analysis, Data Curation, Writing - Review & Editing, Supervision.

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☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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