TIME
IN PHYSICS

Journal for Theoretical, Instrumentation, Material-Molecular, and Education Physics
Volume 1, Issue 1, Pages 1-9 | e-ISSN: 2986-2760|
DOI: 10.11594/timeinphys.2023.v1i1p1-9
ejournal.universitasmandiri.ac.id/index.php/timeinphys

Research Article

Optical Properties of Sodium-doped Carbon Dots Made of Urea and Trisodium Citrate

Isnaeni[1]*, Vivi Purwandari[2], Permono Adi Putro[3], Hammam Magma Adiwidya[4]

[1] Research Center for Photonics, National Research and Innovation Agency, South Tangerang 15314 Indonesia
[2] Department of Chemistry, Faculty of Science and Information Technology, Sari Mutiara University, Medan 20124 Indonesia
[3] Department of Physics, Faculty of Science, Universitas Mandiri, Subang 41211 Indonesia
[4] Department of Chemistry, Bogor Agricultural University, Bogor 16680 Indonesia
*Corresponding Author: isnaeni@brin.go.id

ARTICLE INFO

Article history:
Submitted : 20 December 2022
Revised : 26 January 2023
Accepted : 2 February 2023
Published : 26 February 2023

Keywords:
Carbon dots
Sodium
Microwave
Optical properties
Quantum Yield

ABSTRACT

Carbon dots are very interesting carbon-based nanoparticles. Carbon dots have unique optical properties, especially luminescence properties upon light excitation. Improving optical quality is the challenge in carbon dots research. Doping is one of the methods to improve the quality of carbon dots. In this work, we used sodium, which is an active ion, as doping in the carbon dots. We studied the optical properties of sodium-doped carbon dots. We found that absorbance, FTIR, and photoluminescence spectra changed due additional surface energy level of carbon dots. Furthermore, the quantum yield of carbon dots improved significantly due to sodium doping. In addition, the phosphorescence of sodium-doped carbon dots was slightly longer. Electron behavior was also changed. In conclusion, sodium-doped carbon dots showed very good optical properties for further applications.

Introduction

Carbon dots have emerged as one of the most precious material in nanotechnology because of their magical properties and applications.[1–3] Carbon dots are basically carbon-based nanoparticles, and most of them have an average diameter of less than 10 nm.[4,5] Carbon dots were discovered in 2004, and since then the research development of carbon dots is tremendous due to ease of synthesis and abundant potential applications. Carbon dots can be synthesized from most materials in our daily life. Most of synthesized carbon dots had low quality, which is indicated by quantum efficiency. The quality of carbon dots can be improved by conjugating them with other elements.[6,7] In this case, the synthesis process, and precursors affect the quality of synthesized carbon dots. Carbon dots have the good luminescent property, so that they have the possibility to substitute other nanoparticles, such as quantum dots.[4] In fact, carbon dots are non-toxic, so they can be versatile for many biomedical, biological, and environmental applications.[3] The luminescence of carbon dots become the most interesting property to study.

Luminescent carbon dots have attracted intensive attention from researchers in the fields of photocatalysis, drug delivery, bio-sensing, and cellular imaging, due to their high loading capacity, tunable fluorescence, and low-cost production.[4] Currently, some researchers have shown carbon dots with tunable luminescence from blue to red color.[8,9] Synthesizing the carbon dots with the red, green and blue colors of luminescence can be achieved by varying the carbon sources.[10] Others have tried to tune emission color by doping heteroatoms such as oxygen, nitrogen, phosphorus, sulfur, and boron.[7,11–13] The challenge in carbon dots research is to produce carbon dots that have more photostability, higher quantum yield, more biocompatibility, lower toxicity, more water solubility and better conductivity. Until now, the solid explanation of the origin of the luminescence of carbon dots is still debatable.[4,14] Addition of proper element is considered as one of the best methods. Moreover, there are other elements that can be doped into carbon dots, such as sodium. Sodium may not have optical property; however, the sodium ions may attach to the surface of carbon dots. Only a few studies have been done to observe the influence of sodium on the optical properties of carbon dots.[15,16] Therefore, in this work, we focused on improving the optical properties of carbon dots by studying sodium-doped carbon dots synthesized by a single-step process. We used urea and trisodium citrate to make sodium-doped carbon dots. The purpose of this work was to synthesize sodium-doped carbon dots and to study the origin of enhancement of luminescence of the synthesized carbon dots.

Methodology

We first conducted this work by synthesizing carbon dots, followed by optical characterizations and finally data analysis. There were two samples of carbon dots in this work, which were carbon dots made of urea and ascorbic acid and carbon dots made of urea and trisodium citrate. The characterizations were limited to optical characterization only in this work.

Materials

Urea, ascorbic acid and trisodium citrate were purchased from a local distributor in Indonesia. In this experiment, all chemicals were used without further purification. We used distilled water to dissolve all chemicals.

Research Methods

Carbon dots were made by a simple microwave-assisted technique. Urea (1 gram) was mixed with trisodium citrate (500 mg) in 100 ml distilled water using a magnetic stirrer hotplate (80 ^{o}C, 500 rpm, 30 minutes). The mixture was then placed in a domestic microwave 800 Watt for about 10 minutes until we get brown precipitate. The precipitate was then manually ground using mortal until we get fine power of carbon dots (approximately 10 mg). To get carbon dots in colloid, we dissolved 1 mg of carbon dots powder in 500 ml distilled water and manually stirred. The colloidal carbon dots were then stored overnight before the filtering process was done using Whatman filter paper number 42, to remove the undissolved powder. The sample was then ready for characterization. A similar process was done for carbon dots made of urea and ascorbic acid. The carbon dots made of trisodium citrate and ascorbic acid was then noted as C-ST and C-AA, respectively. For quantum yield measurement, we used 5 ppm Rhodamine 6G as the reference sample.

The characterizations used in this work were UV-Vis-NIR spectrometer using Jasco 760 to measure absorbance spectra and quantum yield, Raman portable system from Horiba using 532 nm (250 mW) wavelength laser excitation to get Raman spectra, 405 nm wavelength laser diode (50 mW) and MAYAPro2000 USB spectrometer to get quantum yield, photoluminescence spectra and phosphorescence. Furthermore, we used Thermo Scientific Nicolet iS-10 to get Fourier-Transform Infrared Spectrometer (FTIR) spectra, and picosecond laser with 420 nm wavelength excitation (60 mW) from Picoquant from time-resolved photoluminescence. For all measurement, we placed the samples in cuvettes.

Data Analysis

Most of the spectra obtained from measurement can be plotted directly using worksheet software. However, two measurements, which were quantum yield and time-resolved photoluminescence, required further analysis. For quantum yield calculation we used the comparison method. We measured the absorbance spectra and photoluminescence spectra of the Rhodamine 6G as the reference sample, as well as carbon dots samples. The quantum yield (QY) was calculated using the following equation.[17]

$$QY = QY_R \times \frac{I_S}{I_R} \times \frac{A_R}{A_S} \tag{1}$$

where I was the photoluminescence intensity, A is the absorbance value at 405 nm wavelength, and index R and S indicated references and sample, respectively. In this case, both carbon dots and Rhodamine 6G were excited using the same laser to get photoluminescence spectra. QY_R for Rhodamine 6G was 95%.[18]

The second measurement that required data analysis was time-resolved photoluminescence. The decay lifetime curve was fitted using a double exponential decay equation as follows.[19]

$$Y = A_0 + A_1 \exp\left({}^{-t}/_{\tau_1}\right) + A_2 \exp\left({}^{-t}/_{\tau_2}\right) \tag{2}$$

The decay lifetime of each term produced fitting parameters τ and A. The average decay lifetime was then calculated using the following equation.[19]

$$\tau_{average} = \sum_{n=1}^{2} \frac{A_n \tau_n^2}{A_n \tau_n} \tag{3}$$

Results and Discussion

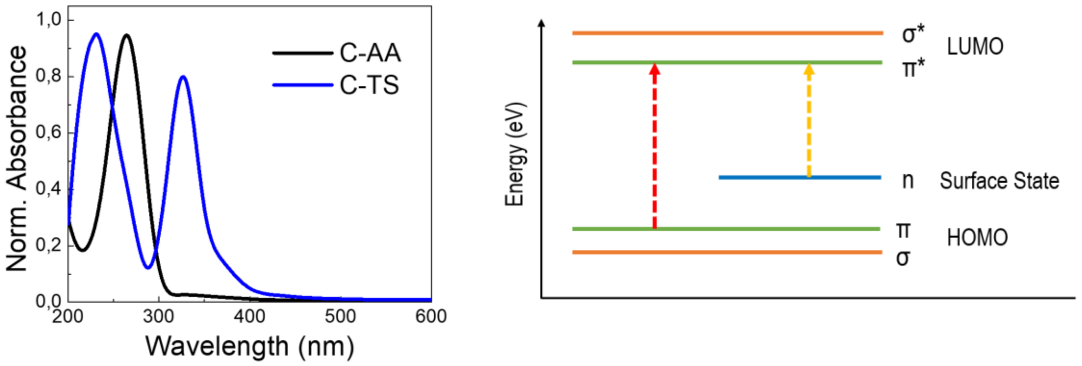
Carbon dots were successfully synthesized using a microwave-assisted technique. The appearance of synthesized carbon dots in cuvettes was shown in Figure 1. Carbon dots made of urea and ascorbic acid (C-AA) showed light brown color. Meanwhile, carbon dots made of urea and trisodium citrate (C-ST) showed greenish-brown color. Different colors of carbon dots indicated the structure and functional group on the surface of carbon dots were not the same. In this work, we used urea (CH_4N_2O) as one of the precursors. Urea consisted of C, N, H, and O atoms. For carbon dots C-AA, we used ascorbic acid ($C_6H_8O_6$), which also consisted of C, H, and O atoms. On the other hand, sample carbon dots C-ST used trisodium citrate ($Na_3C_6H_5O_7$), so there was an additional sodium atom in the carbon dots sample. We assumed that the sodium atom affected the appearance of carbon dots and optical properties that will be discussed further in this work. Furthermore, the colloidal carbon dots synthesized in this work were very stable for more than 3 months in the ambient atmosphere. We observed that there was no sedimentation on the bottom of the storage bottle after 3 months. The color of the carbon dots also remained the same. This indicated that our synthesized carbon dots were very stable and were able to be utilized for potential applications.

(a) (b)

Figure 1. (a) Carbon dots made of urea and ascorbic acid (C-AA) and carbon dots made of urea and trisodium citrate (C-ST). (b) green emission from synthesized carbon dots.

In addition, the unique optical property of carbon dots was the luminescence upon blue light excitation. Figure 1b showed the green emission from carbon dots (C-ST) when the carbon dots were excited by green laser 405 nm wavelength. The same green emission was also observed for carbon dots C-AA. The green emission from our carbon dots was strong and noticeable to the naked eye. The strong emission was related to the quantum yield of carbon dots, which will be discussed later in this work.

In order to clarify the difference between two carbon dots samples, which were C-AA and C-ST, we started to characterize the absorbance spectra of carbon dots samples using a UV-Vis-NIR spectrometer. Figure 2a showed the normalized absorbance spectra of carbon dots C-AA (black line) and carbon dots C-ST (blue line). The absorbance spectrum of carbon dots C-AA was different from that of carbon dots C-ST. In the C-AA spectrum, we found one main absorbance peak at 264 nm and a low absorbance peak at 340 nm. On the other hand, there were two strong absorbance peaks in carbon dots C-ST spectrum at 230 nm and 325 nm. The difference in absorbance spectra was probably due sodium atom in the carbon dots. In general, we were able to classify the absorbance peak of carbon dots into two types. The first peak was due to π to π^* energy transition as shown by a dotted-red arrow in Figure 2b. This transition required high energy, since the electrons from π energy state in the highest occupied molecular orbital (HOMO) must be excited to π^* energy state in the lowest unoccupied molecular orbital (LUMO). This energy transition is related to the C=C bond in the carbon dots.[2] In the absorbance spectra, the π to π^* energy transition was noted at wavelength 264 nm (equal to 4.7 eV) for C-AA and at wavelength 230 nm (equal to 5.4 eV) for C-ST. In this case, we found that the π to π^* energy transition for each carbon dots sample may be different. In addition, there was another energy transition in the carbon dots. This was the n to π^* energy transition.[2,8] This is the uniqueness of carbon-based nanostructure. The n state was the surface energy state due interaction between atom C to other atoms, such as O, H, and N, at the surface of carbon dots.[7] This energy transition in noted as a dotted-orange arrow in Figure 2b. In the absorbance spectra, the n to π^* energy transition was noted at wavelength 340 nm (equal to 3.6 eV) for C-AA and at wavelength 350 nm (equal to 3.5 eV) for C-ST. In this case, we found that the n to π^* energy transition for each carbon dots samples was similar. From absorbance spectra, we found that the surface energy transition of sample carbon dots C-ST was more dominant than that of carbon dots C-AA.



(a) (b)

Figure 2. Absorbance spectra of carbon dots (a) and schematic explanation of energy transition in carbon dots (b).

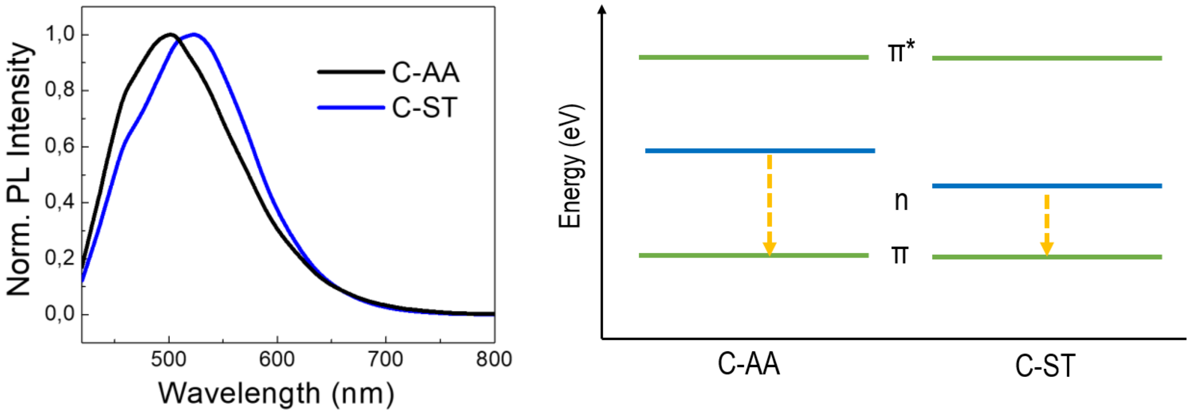
High energy transition of carbon dots C-ST can influence other optical properties of carbon dots. Next, we studied the quantum yield (QY) of carbon dots. QY actually indicates how efficiently carbon dots emit light. QY was the ratio of the photon energy of emitted light to the photon energy of absorbed light.[17] In this work, we used a comparison method to calculate QY based on Equation 1. Table 1 showed the absorbance value and total integrated photoluminescence. The value of absorbance was taken from the original spectra of Figure 2a, and total integrated photoluminescence was calculated from the original spectra of Figure 3a. The QY of carbon dots C-ST was 12.9%. This value was much higher than the QY of carbon dots C-AA, which was only 1.7%. The value of QY 12.9% was actually high compared to other research. The QY of carbon dots may vary from 1% to 45%.[20] High QY value is strongly related to a high absorbance peak of n to π^* energy transition of carbon dot sample C-ST.

The sodium addition to carbon dots in our work may result in higher QY. Interaction between sodium and C and other atoms generated new surface-level energy. This new energy level become the preferred energy level for the electrons to stay for a while before the radiative recombination process, which emitted light. The addition of a new surface energy level also increased the number of electrons that can be excited from HOMO to LUMO energy levels. More excited electrons mean more possibility for carbon dots to emit light by the radiative recombination process.

Table 1.

Sample	Absorbance @λ=405nm	Integrated Photoluminescence Range λ 410-800 nm (counts)	Quantum Yield (%)
Rhodamine 6G	0,014	$0,49 \times 10^6$	95 (Ref)
C-AA	1,326	$1,95 \times 10^6$	1.7
C-ST	0,971	$4,61 \times 10^6$	12.9

In most cases, high QY may contribute to the changes in the photoluminescence spectrum as shown in Figure 3a. In this figure, we normalized the photoluminescence spectra to make an easy comparison. For information, the photoluminescence intensity was proportional to the integrated photoluminescence value in Table 1. The photoluminescence intensity of carbon dots C-ST was more than two times of photoluminescence intensity of carbon dot C-AA. From Figure 3a we can see that the photoluminescence peak of carbon dots C-ST was at 522 nm (equal to 2.4 eV). Meanwhile, carbon dots S-AA has a photoluminescence peak at 501 nm (equal to 2.5 eV). In addition, both C-AA and C-ST had shoulder peaks at 459 nm. From photoluminescence spectra, we assumed that the emission of carbon dots C-ST was red-shift. It means that electrons preferred to radiatively recombined at lower energy levels. The possible schematic explanation was shown in Figure 3b. The dotted-yellow arrows were the radiative recombination process. The surface energy level (*n*) of carbon dots C-ST was lower than that of carbon dots C-AA. Thus, the radiative recombination of carbon dots C-ST generated emission to shift to red color or longer wavelength. We assumed this lower energy level in carbon dots C-ST was strongly related to the addition of sodium in the carbon dots sample.



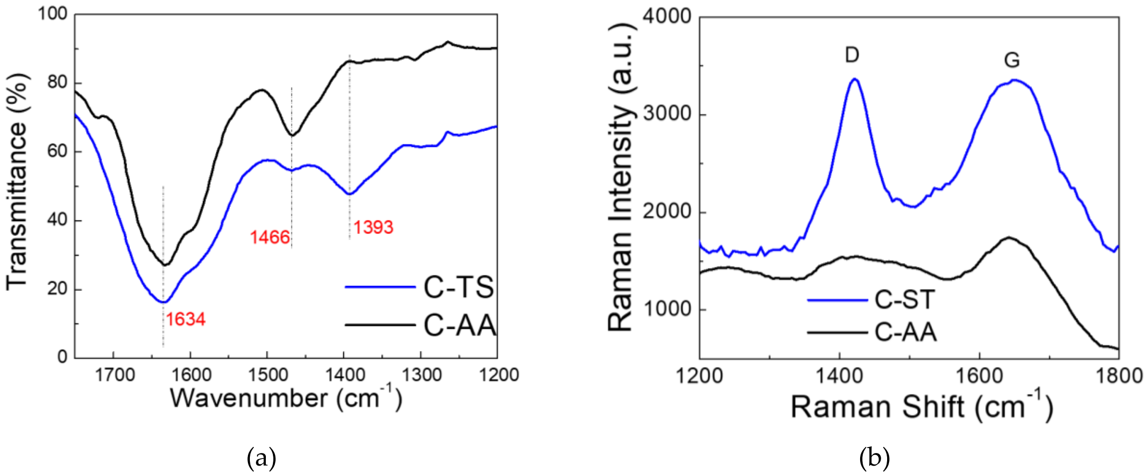
(a) (b)

Figure 3. Photoluminescence spectra of carbon dots (a) and schematic explanation of radiative recombination (b).

So far, we have shown evidences of sodium-doped carbon dots. Furthermore, the presence of sodium in the carbon dots can be noticed from the FTIR spectrum as shown in Figure 4a. Basically, the FTIR spectrum of carbon dots C-AA and C-ST were similar except for one peak only. FTIR peak at 1634 cm^{-1} wavenumber indicated the C=O vibration in amide group of carbon dots.[21] FTIR peak at 1466 cm^{-1} wavenumber could be assigned to the symmetrical and asymmetrical stretching of nitrogen group.[12] The FTIR peak 1393 cm^{-1} wavenumber was strongly noticed only at sample carbon dots C-ST. This peak was related to C–O and C=O stretching vibrations of sodium carboxyl groups.[21] One had shown that sodium ions were doped into C atoms in the carbon dots by making sodium carboxyl group Na-C-O.[15,16] This FTIR spectrum was evidence of sodium-doped carbon dots.

The influence of sodium in our carbon dots also can be also seen in Raman spectra as shown in Figure 4b. Similar to other carbon-based nanostructures, such as graphene and carbon nanotubes, Raman spectra of carbon dots show two important peaks. The first peak is at 1421 cm^{-1}, and the second peak is at 1647 cm^{-1}. The first peak was related to the defect structure of carbon dots, noted by symbol D.[22] The defect can be located on the surface of the inside carbon dots. The second peak was noted as G, which indicated the crystalline structure of carbon dots. In our work, we found that sample carbon dots had strong D peaks. Therefore, we can assume that defects in the carbon dots and functional groups on the surface of carbon dots had been increased. This was probably related to sodium atoms in the carbon dots.

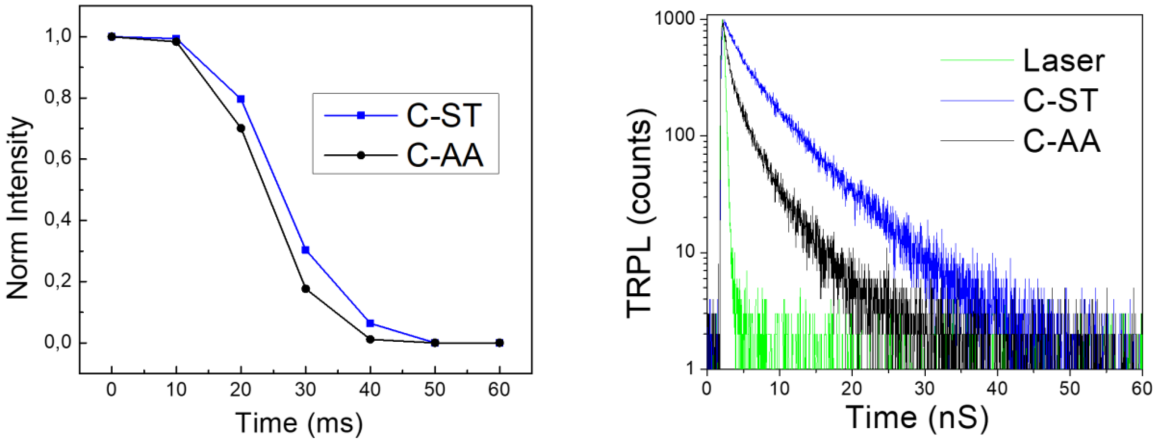
So far, we have observed the influence of sodium as a doping atom in carbon dots. Next, we would like to observe the phosphorescence of carbon dots. We recorded the emission intensity of carbon dots after the excitation laser was turned off as shown in Figure 5a. We found that carbon dots C-ST have longer phosphorescence than carbon dots C-AA. Carbon dot C-ST could stay 10 ms longer than that of carbon dots C-AA. In our work, we found that carbon dots C-ST stayed emitting light until 50 ms after the excitation laser was turned off.



(a) (b)

Figure 4. FTIR spectra (a) and Raman spectra (b) of carbon dots.

Finally, we evaluated the electron behavior of carbon dots using time-resolved photoluminescence as shown in Figure 5b. In this experiment, we measured electron lifetime starting from the time when the electron was excited from HOMO to LUMO until the electron returned to HOMO by radiative recombination process. We found that carbon dots C-ST had a longer electron lifetime, 4.6 ns. Carbon dots C-AA only had an electron lifetime of 2.8 ns. From this experiment, we assumed that the longer electron lifetime of carbon dots C-ST was related to the addition surface energy level due to sodium addition.



(a) (b)

Figure 5. Phosphorescence (a) and time-resolved photoluminescence (b) of carbon dots.

Conclusion

We have successfully synthesized sodium-doped carbon dots using a simple microwave-assisted technique. The synthesized carbon dots had a strong luminescence, since the quantum yield was 12.9%. We noticed that surface energy levels were strongly noticed in absorbance, FTIR and Raman spectra. This indicated that sodium was doped in the carbon dots structure. In addition, the phosphorescence of sodium-doped carbon dots was 50 ms and the electrons also preferred to stay longer in the surface levels. We found that the addition of sodium in our carbon dots may produce good optical properties.

Funding

This work was fully supported by the 18th Science and Technology Research Grant Tahun 2022 Indonesia Toray Science Foundation, Research Grant number 021/XII/ITSF/SEK/2021.

Acknowledgement

All experiments were conducted in Research Center for Photonics BRIN with the full support of characterization equipment provided by e-layanan sains (ELSA) BRIN.

Conflicts of Interest

The authors whose names are listed above certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

Author Contribution

Isnaeni: Research idea, research planning, data analysis and manuscript writing. **Vivi Purwandari**: Sample preparation and data analysis. **Permono Adi Putro**: Characterizations. **Hammam Magma Adiwidya**: Data analysis for quantum yield.

References

1. Kang C, Huang Y, Yang H, Yan XF, Chen ZP. A Review of carbon dots produced from biomass wastes. *Nanomaterials*. 2020;10(11):2316. doi:10.3390/nano10112316
2. Isnaeni, Herbani Y, Suliyanti MM. Concentration effect on optical properties of carbon dots at room temperature. *Journal of Luminescence*. 2018;198:215-219. doi:10.1016/j.jlumin.2018.02.012
3. Sharma A, Das J. Small molecules derived carbon dots: synthesis and applications in sensing, catalysis, imaging, and biomedicine. *J Nanobiotechnol*. 2019;17(1):92. doi:10.1186/s12951-019-0525-8
4. Wang X, Feng Y, Dong P, Huang J. A mini review on carbon quantum dots: preparation, properties, and electrocatalytic application. *Front Chem*. 2019;7:671. doi:10.3389/fchem.2019.00671
5. Zhao B, Tan Z. Fluorescent carbon dots: Fantastic electroluminescent materials for light-emitting diodes. *Advanced Science*. 2021;8(7):2001977. doi:10.1002/advs.202001977
6. Li X, Fu Y, Zhao S, et al. Metal ions-doped carbon dots: Synthesis, properties, and applications. *Chemical Engineering Journal*. 2022;430:133101. doi:10.1016/j.cej.2021.133101
7. Li F, Yang D, Xu H. Non-metal-heteroatom-doped carbon dots: Synthesis and properties. *Chemistry – A European Journal*. 2019;25(5):1165-1176. doi:10.1002/chem.201802793
8. Ai L, Yang Y, Wang B, et al. Insights into photoluminescence mechanisms of carbon dots: advances and perspectives. *Science Bulletin*. 2021;66(8):839-856. doi:10.1016/j.scib.2020.12.015
9. Liu M. Optical properties of carbon dots: A review. *NAT*. 2020;1(1):1-12. doi:10.37256/nat.112020124.1-12
10. Zhu Z, Zhai Y, Li Z, et al. Red carbon dots: Optical property regulations and applications. *Materials Today*. 2019;30:52-79. doi:10.1016/j.mattod.2019.05.003

11. Kurdekar A, Chunduri LAA, Bulagonda EP, Haleyurgirisetty MK, Kamisetti V, Hewlett IK. Comparative performance evaluation of carbon dot-based paper immunoassay on Whatman filter paper and nitrocellulose paper in the detection of HIV infection. *Microfluid Nanofluid*. 2016;20(7):99. doi:10.1007/s10404-016-1763-9
12. Karaman C. Orange peel derived-nitrogen and sulfur co-doped carbon dots: A nano-booster for enhancing ORR electrocatalytic performance of 3D graphene networks. *Electroanalysis*. 2021;33(5):1356-1369. doi:10.1002/elan.202100018
13. Atchudan R, Edison TNJI, Perumal S, Muthuchamy N, Lee YR. Hydrophilic nitrogen-doped carbon dots from biowaste using dwarf banana peel for environmental and biological applications. *Fuel*. 2020;275:117821. doi:10.1016/j.fuel.2020.117821
14. Liu Y, Huang H, Cao W, Mao B, Liu Y, Kang Z. Advances in carbon dots: from the perspective of traditional quantum dots. *Mater Chem Front*. 2020;4(6):1586-1613. doi:10.1039/D0QM00090F
15. Lin Z, Yang J, Zeng Q, Tie S, Huang R, Lan S. Deep blue photoluminescence and optical gain from sodium-doped carbon dots. *Journal of Luminescence*. 2022;246:118856. doi:10.1016/j.jlumin.2022.118856
16. Velusamy J, Ramos-Ortiz G. Na-doped carbon nanodots: shed light on the concentration modulated photoluminescence and two-photon absorption performance. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2022;634:127993. doi:10.1016/j.colsurfa.2021.127993
17. Hu J, Zhang C yang. Simple and accurate quantification of quantum yield at the single-molecule/particle level. *Anal Chem*. 2013;85(4):2000-2004. doi:10.1021/ac3036487
18. Fischer M, Georges J. Fluorescence quantum yield of rhodamine 6G in ethanol as a function of concentration using thermal lens spectrometry. *Chemical Physics Letters*. 1996;260(1-2):115-118. doi:10.1016/0009-2614(96)00838-X
19. Li Y, Natakorn S, Chen Y, et al. Investigations on average fluorescence lifetimes for visualizing multi-exponential decays. *Front Phys*. 2020;8:576862. doi:10.3389/fphy.2020.576862
20. Yi Z, Li X, Zhang H, et al. High quantum yield photoluminescent N-doped carbon dots for switch sensing and imaging. *Talanta*. 2021;222:121663. doi:10.1016/j.talanta.2020.121663
21. Xu D, Li M, Xu H, Yu J, Wang Y, Zhang P. N,S-doped carbon quantum dots as a fluorescent probe for palladium(II) ions via Förster resonance energy transfer. *Results in Chemistry*. 2021;3:100179. doi:10.1016/j.rechem.2021.100179
22. Dervishi E, Ji Z, Htoon H, Sykora M, Doorn SK. Raman spectroscopy of bottom-up synthesized graphene quantum dots: size and structure dependence. *Nanoscale*. 2019;11(35):16571-16581. doi:10.1039/C9NR05345J