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THE EFFECT OF POLY (ETHYLENE GLYCOL) ON THE PHOTOLUMINESCENCE PROPERTIES OF CARBON DOTS FROM CASSAVA PEELS SYNTHESIZED BY HYDROTHERMAL METHODS

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ABSTRACT

Carbon dots (C-dots) have been successfully synthesized from cassava peels using the hydrothermal method. The C-dots are further passivated using poly (ethylene glycol) (PEG) with a variation of the volume of 0.5 ml, 1.0 ml, and 1.5 ml. The properties of photoluminescence C-dots before and after PEG were characterized using photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectrophotometers. PEG succeeded in influencing PL C-dots properties, such as peak wavelength, PL intensity, and electron time decay. The addition of 0.5 ml of PEG to C-dots is the optimum condition and best with the peak wavelength, the PL intensity and, time decay electron is 507.52 nm, 5302 a.u, and 3.794031133 ns, respectively.

Keywords: carbon dots, cassava peels, photoluminescence

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INTRODUCTION

Carbon dots (C-dots) have emerged recently as one of the most interesting discoveries in the search for new nanomaterials [1,2]. C-dots was discovered accidentally in 2004 as one of the substances produced by the purification or purification of a type of single-walled carbon nanotubes (SWNT) [3]. C-dots are nanoparticles that emit light or fluoresce, are not toxic compared to similar alternatives such as quantum dots [2]. C-dots are materials belonging to the class of 0-dimensional nanoparticles that have photoluminescence (PL) properties [4] with a size below 10 nm, having an sp² hybridized carbon atom structure with abundant oxygen residues [5] and their surfaces coated with oxygen groups, polymer, or other species [6,7].

The development in making C-dots using natural materials that have carbon chain bonds is a challenge and very rapid progress [8]. This is because the optical properties of C-dots from natural sources or chemicals have comparable purity [9]. Some natural ingredients that have been made C-dots, as flowers [10], fruit [11], fruit peels [12,13], vegetables [14], and leaves [15]. C-dots can be synthesized by several methods, as laser ablation [16], electrochemical [17], arc-discharge [3], ultrasonic [18], and microwave [13]. This method has several advantages, such as facile, fast, measurable and tunable surface conditions [19]. However, all the methods mentioned above at some level have disadvantages, such as complex and time-consuming process requirements, high temperatures and complicated synthetic conditions [20]. Recently, hydrothermal is a method of synthesis of C-dots that is needed because it has environmentally friendly features without strong acids or organic reagents in the process. The resulting C-dots dissolve easily in water to form stable, yellow, and transparent aqueous solutions without precipitation for months [21].

Zhu *et al.* show that C-dots formed from glucose that is PEG-passivated directly in the synthesis process produce mono-dispersion C-dots. According to them, PEG acts only as a passivating agent that coats the surface of C-dots resulting in different PL properties [22]. However, according to Jaiswal *et al.* the role of PEG in Zhu *et al.* research. It is still unclear the carbon source in C-dots comes from glucose, PEG or both because the passivation process is carried out directly in the synthesis process [23]. Therefore, we synthesize C-dots from cassava peel using the hydrothermal method and surface passivation with PEG. Furthermore, C-dots before and after PEG were characterized using PL spectrophotometers and TRPL to study the PL properties of C-dots.

RESEARCH METHOD

This research was carried out through several steps, such as synthesis and surface passivation of C-dots with PEG. This research scheme can be seen in FIGURE 1.



FIGURE 1. The schematic synthesis and passivation surface of C-dots with PEG.

Synthesis of C-dots

The 10 gr of cassava peels crush using a blender with 100 ml of aquadest as a solvent. The cassava peels solution is filtered to get the extract which will be used as a precursor for the synthesis of C-dots. 30 ml of precursor solution was put into the autoclave Teflon and heated using an oven at a temperature of 160°C for 4 hours. The solution obtained was then filtered using 40 mesh filter paper to separate carbon precipitation and C-dots. Furthermore, the solution obtained from the filtration was centrifuged with 10000 rpm for 10 minutes to separate the remaining carbon precipitation and agglomerated particles to obtain clear colloids.

Addition of PEG in C-dots

The 0.2 ml of C-dots are put into a beaker and heated use hotplate at a temperature of 100°C for 10 minutes so that the colloidal C-dots dried. Next, PEG with a volume variation of 0.5 ml, 1.0 ml, and 1.5 ml and heated at 100°C for 5 minutes. Furthermore, 10 ml of aquadest to disperse C-dots and PEG, respectively.

Characterization

The PL C-dots were measured using a picosecond diode laser at a wavelength of 420 nm as a source of excitation. C-dots emissions are collected and directed to the PL detector using a beam splitter. PL C-dots spectrum data were obtained using the Spectra Suite software. Meanwhile, TRPL C-dots are measured using laser pulses as a source of their existence with a Micro Photon Devices (MPD) detector. C-dots emissions are directed to the TRPL detector

using a beam splitter and are blocked using a 500 nm long pass filter. Electron all-time data obtained using software Time Harp 260. Settings in PL and TRPL C-dots measurements can be seen in FIGURE 2 [24].



FIGURE 2. The measure set up of PL and TRPL.

Measurement of Life Time

All samples characterized using laser pulses on laser drivers and 500 nm long pass filters were then recorded using the TRPL detector to determine the electron time decay of C-dots. The electron time decay of C-dots can be obtained from the fitting decay curve which satisfies the multi-exponential decay function as in EQ. (1) as follows [25–27]:

$$I(t) = \sum_{i} a_{i} \exp\left(\frac{-t}{\tau_{i}}\right)$$

$$\tau_{i} = \frac{\sum_{i} a_{i} \tau_{i}^{2}}{\sum_{i} \tau_{i}^{2}}$$

$$(1)$$

$$\tau_i = \frac{1}{\sum a_i \tau_i}$$
(2)

Where a_i and τ_i are multi-exponential decay components of amplitude and lifetime. The measurement of the average lifetime of C-dots can be obtained using EQ. (2) [26–30].

RESULTS AND DISCUSSION

The PL is the emission or emission of light from an excited state in an electronic transition spontaneously after absorbing light. The PL process can be observed in the position of the spectrum, dynamics, and efficiency in obtaining relevant information. The spectrum provides information about the energy difference between the excited state and the ground state which serves as the first indicator of material application [31].



FIGURE 3. The PL spectrum of colloidal C-dots with an excitation 420 nm wavelength.



FIGURE 4. The curve of correlation between peak PL intensity and wavelength of C-dots

All types of C-dots have emissions at the PL wavelength independently of the excitation wavelength [7]. The PL spectrum of C-dots colloid synthesized using the 4-hour hydrothermal method and PEG-passivated can be seen in FIGURE 3. The peak PL wavelength is maximum colloid C-dots and C-dots/PEG with variations of 0.5 ml, 1.0 ml, and 1.5 ml respectively 484.13 nm, 507.52 nm, 508.90 nm, and 509.82 nm with PL intensities of 223 au, 5302 au, 4977 au, and 4716 au respectively. It is worth mentioning that the shift in emission peak of CDs is an indication of multicolor fluorescence [32].

The peak of the PL wavelength spectrum when PEG addition shows the redshift. The peak of PL intensity when adding 0.5 ml of PEG increased sharply, but when adding 1.0 ml, and 1.5 ml PEG decreased. The relationship between peak intensity and maximum PL wavelength can be seen in FIGURE 4. The shift in peak wavelength and maximum PL intensity observed at

peak PL intensity is ascribed to the carboxyl group and the degree of oxidation on the surface structure and not from particle size. It means that the PL C-dots are not like quantum dots semiconductors. Surface oxidation serves as the center of exciton capture to produce PL that is related to surface conditions. Higher oxidation levels on the surface of C-dots, which show more surface defects [33]. Besides, we assume that the difference in PL C-dots intensity is due to the molecular density and content of the preparation [33,34].

The electron time decay is an essential characteristic of light emitting nanoparticles. The time difference of all electrons corresponds to different electron-hole recombination mechanisms [35]. Electron time decay measurements are used to determine the PL properties that show some energy levels of C-dots [36]. The electron time measurements are carried out under the excitation pulse, and its decay is recorded after the excitation pulse ends [31]. The curve of electron time decay of C-dots and C-dots/PEG can be seen in FIGURE 5. For all samples, the decay curves can be fitted to a triple exponential function, which suggests the presence of multi-radiative species [32]. Electron time decay of C-dots before and after passivated of PEG with variations in the volume of 0.5 ml, 1.0 ml and 1.5 ml which are 4.072503765 ns, 3.794031133 ns, 3.798995187 ns, and 3,81977658 ns, respectively. Such shorter lifetimes indicate radiative recombination of excitations [37].

The PL spectrum position at the maximum intensity and time of all electrons in the C-dots colloid is related to the PL mechanism. The relationship of PL intensity and time of decay of electron C-dots can be seen in FIGURE 6. PL intensity influences the time of electrons in the colloidal C-dots. PL intensity increased at the addition of 0.5 mg/ml PEG and decreased when adding 1.0 mg/ml and 1.5 mg/ml PEG according to the time of all electrons. The short time of all electrons can show that the electrons directly return to the valence band in pulsed laser excitation. Meanwhile, the longer time of all electrons indicates that there may be an additional energy level between the valence and the conduction band. The short electron shedding time means high emission efficiency [38]. In this case, C-dots that are passivated by PEG show the longer the time of the electrons. In addition to PL intensities that can affect the time of electron shedding, changes in molecular functional groups (such as bond breaking) also affect emitters due to oxidation, aging and other modifications of organic molecules [39].



FIGURE 5. The curve of electron time decay of C-dots and C-dots/PEG.



FIGURE 6. The correlation between PL intensity and electron time decay of C-dots

CONCLUSIONS

The addition of PEG with variations in the volume of 0.5 ml, 1.0 ml, and 1.5 ml on C-dots affected the peak wavelength, PL intensity and time of electrons. The addition of 0.5 ml of PEG to C-dots is the optimum condition and best with the peak wavelength at 507.52 nm, PL intensity at 5302 a.u, and the time of all electrons at 3.794031133 ns. These results provide the potential for C-dots/PEG in aqueous solutions to be applied as biological imaging and biosensing. However, additional optical measurements, bonding, and chemical composition, and particle structure are needed to support our findings.

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REFERENCES

- [1] J. Yu, J. Nan, and H. Zeng, "Size control of nanoparticles by multiple-pulse laser ablation," Appl. Surf. Sci., vol. 402, pp. 330–335, 2017.
- [2] M. Algarra, et al., "Luminescent carbon nanoparticles: Effects of chemical functionalization, and evaluation of Ag+ sensing properties," J. Mater. Chem. A, vol. 2, no. 22, pp. 8342–8351, 2014.
- [3] X. Xu, et al., "Electrophoretic analysis and purification of fluorescent single-walled carbon nanotube fragments," J. Am. Chem. Soc., vol. 126, no. 40, pp. 12736–12737, 2004.

- [4] S. Sugiarti and N. Darmawan, "Synthesis of Fluorescence Carbon Nanoparticles from Ascorbic Acid," Indonesian Journal of Chemistry, 15(2), pp. 141-145, 2015.
- [5] Y. Fang, et al., "Easy synthesis and imaging applications of cross-linked green fluorescent hollow carbon nanoparticles," ACS Nano, vol. 6, no. 1, pp. 400–409, 2012.
- [6] V. Strauss, et al., "Carbon nanodots: Toward a comprehensive understanding of their photoluminescence," J. Am. Chem. Soc., vol. 136, no. 49, pp. 17308–17316, 2014.
- [7] L. Bao, C. Liu, Z. L. Zhang, and D. W. Pang, "Photoluminescence-tunable carbon nanodots: Surface-state energy-gap tuning," Adv. Mater., vol. 27, no. 10, pp. 1663– 1667, 2015.
- [8] P. Z. Z. Ngu, S. P. P. Chia, J. F. Y. Fong, and S. M. Ng, "Synthesis of carbon nanoparticles from waste rice husk used for the optical sensing of metal ions," New Carbon Mater., vol. 31, no. 2, pp. 135–143, 2016.
- [9] Isnaeni, I. Rahmawati, R. Intan, and M. Zakaria, "Photoluminescence study of carbon dots from ginger and galangal herbs using microwave technique," J. Phys. Conf. Ser., no. 985, p. 012004, 2018.
- [10] W. Liu, H. Diao, H. Chang, H. Wang, T. Li, and W. Wei, "Green synthesis of carbon dots from rose-heart radish and application for Fe3+ detection and cell imaging," Sensors Actuators B Chem., vol. 241, pp. 190–198, 2017.
- [11] A. Tadesse, D. R. Devi, M. Hagos, G. R. Battu, and K. Basavaiah, "Facile green synthesis of fluorescent carbon quantum dots from citrus lemon juice for live cell imaging," Asian J. Nanosci. Mater., vol. 1, no. 1, pp. 36–46, 2018.
- [12] P. A. Putro, L. Roza, and Isnaeni, "Karakterisasi sifat fotoluminisensi C-dots dari kulit ari singkong menggunakan teknik microwave," Pros. Semin. Nas. Fis. FMIPA UNESA, vol. 2, pp. 168–173, 2018.
- [13] P. A. Putro, L. Roza, and Isnaeni, "Karakterisasi sifat optik C-dots dari kulit luar singkong menggunakan teknik microwave," J. Teknol. Technoscientia, vol. 11, no. 2, pp. 128–136, 2019.
- [14] A. M. Alam, B. Y. Park, Z. K. Ghouri, M. Park, and H. Y. Kim, "Synthesis of carbon quantum dots from cabbage with down- and up-conversion photoluminescence properties: Excellent imaging agent for biomedical applications," Green Chem., vol. 17, no. 7, pp. 3791–3797, 2015.
- [15] A. Kumar, A. R. Chowdhuri, D. Laha, T. K. Mahto, P. Karmakar, and S. K. Sahu, "Green synthesis of carbon dots from Ocimum sanctum for effective fluorescent sensing of Pb2+ ions and live cell imaging," Sensors Actuators B Chem., vol. 242, pp. 679–686, 2017.
- [16] H. P. S. Castro, M. K. Pereira, V. C. Ferreira, J. M. Hickmann, and R. R. B. Correia, "Optical characterization of carbon quantum dots in colloidal suspensions," Opt. Mater. Express, vol. 7, no. 2, pp. 5801–5806, 2017.
- [17] L. Zheng, Y. Chi, Y. Dong, J. Lin, and B. Wang, "Electrochemiluminescence of watersoluble carbon nanocrystals released electrochemically from graphite," J. Am. Chem. Soc., vol. 131, no. 13, pp. 4564–4565, 2009.

- [18] H. Li, X. He, Y. Liu, H. Huang, S. Lian, S. T. Lee, and Z. Kang, "One-step ultrasonic synthesis of water-soluble carbon nanoparticles with excellent photoluminescent properties," Carbon N. Y., vol. 49, no. 2, pp. 605–609, 2011.
- [19] M. Farshbaf, S. Davaran, F. Rahimi, N. Annabi, R. Salehi, and A. Akbarzadeh, "Carbon quantum dots: Recent progresses on synthesis, surface modification, and applications," Artif. Cells, Nanomedicine, Biotechnol., vol. 46, no. 7, pp. 1331–1348, 2017.
- [20] S. Sahu, B. Behera, T. K. Maiti, and S. Mohapatra, "Simple one-step synthesis of highly luminescent carbon dots from orange juice: application as excellent bio-Imaging agents," Chem. Commun., vol. 48, no. 70, pp. 8835–8837, 2012.
- [21] A. Prasannan and T. Imae, "One-pot synthesis of fluorescent carbon dots from orange waste peels," Ind. Eng. Chem. Res., vol. 52, no. 44, pp. 15673–15678, 2013.
- [22] H. Zhu, X. Wang, Y. Li, Z. Wang, F. Yang, and X. Yang, "Microwave synthesis of fluorescent carbon nanoparticles with electrochemiluminescence properties," Chem. Commun., vol. 4, no. 34, pp. 5118–5120, 2009.
- [23] A. Jaiswal, S. S. Ghosh, and A. Chattopadhyay, "One step synthesis of C-dots by microwave mediated caramelization of poly(ethylene glycol)," Chem. Commun., vol. 48, no. 3, pp. 407–409, 2012.
- [24] Isnaeni, M. Y. Hanna, A. A. Pambudi, and F. H. Murdaka, "Influence of ablation wavelength and time on optical properties of laser ablated carbon dots," AIP Conf. Proc., vol. 1801, no. 020001, pp. 1–5, 2017.
- [25] Q. Li, M. Zhou, M. Yang, Q. Yang, Z. Zhang, and J. Shi, "Induction of long-lived room temperature phosphorescence of carbon dots by water in hydrogen-bonded matrices," Nat. Commun., vol. 9, no. 734, pp. 1–8, 2018.
- [26] J. R. Lakowicz, Principles of Fluorescence Spectroscopy. Springer US, 2006.
- [27] T. Yoshinaga, Y. Iso, and T. Isobe, "Particulate, structural, and optical properties of Dglucose-derived carbon dots synthesized by microwave-assisted hydrothermal treatment," ECS J. Solid State Sci. Technol., vol. 7, no. 1, pp. R3034–R3039, 2018.
- [28] X. Dong, L. Wei, Y. Su, Z. Li, H. Geng, C. Yang, and Y. Zhang, "Efficient long lifetime room temperature phosphorescence of carbon dots in a potash alum matrix," J. Mater. Chem. C, vol. 3, February, pp. 2798–2801, 2015.
- [29] M. Chang, L. Li, H. Hu, Q. Hu, A. Wang, and X. Cao, "Using fractional intensities of time-resolved fluorescence to sensitively quantify NADH/NAD + with genetically encoded fluorescent biosensors," Sci. Rep., vol. 7, no. 4209, pp. 1–9, 2017.
- [30] Z. L. Wu, P. Zhang, M. X. Gao, C. F. Liu, W. Wang, F. Leng, and C. Z. Huang, "Onepot hydrothermal synthesis of highly luminescent nitrogen-doped amphoteric carbon dots for bio-imaging from Bombyx mori silk-natural proteins," J. Mater. Chem. B, no. 22, pp. 2868–2873, 2013.
- [31] O. Kozák, M. Sudolská, G. Pramanik, P. Cígler, M. Otyepka, and R. Zbořil, "Photoluminescent carbon nanostructures," Chem. Mater., vol. 28, no. 12, pp. 4085– 4128, 2016.
- [32] A. Sachdev, I. Matai, and P. Gopinath, "Implications of surface passivation on physicochemical and bioimaging properties of carbon dots," RSC Adv., vol. 4, no. 40, pp. 20915–20921, 2014.

- [33] H. Ding, S. B. Yu, J. S. Wei, and H. M. Xiong, "Full-color light-emitting carbon dots with a surface-state-controlled luminescence mechanism," ACS Nano, vol. 10, no. 1, pp. 484–491, 2016.
- [34] S. Fatimah, Isnaeni, and D. Tahir, "Sintesis dan karakterisasi fotoluminisens carbon dots berbahan dasar organik dan limbah organik," POSITRON, vol. VII, no. 2, pp. 37–41, 2017.
- [35] X. Zhang, Y. Zhang, Y. Wang, S. Kalytchuk, S. V. Kershaw, Y. Wang, P. Wang, T. Zhang, Y. Zhao, H. Zhang, T. Cui, Y. Wang, J. Zhao, W. W. Yu, and A. L. Rogach, "Color-switchable electroluminescence of carbon dot light-emitting diodes," ACS Nano, vol. 7, no. 12, pp. 11234–11241, 2013.
- [36] B. P. Jiang, Y. X. Yu, X. L. Guo, Z. Y. Ding, B. Zhou, H. Liang, and X. C. Shen, "Whiteemitting carbon dots with long alkyl-chain structure: Effective inhibition of aggregationcaused quenching effect for label-free imaging of latent fingerprint," Carbon N. Y., vol. 128, pp. 12–20, 2018.
- [37] S. K. Bhunia, A. Saha, A. R. Maity, S. C. Ray, and N. R. Jana, "Carbon nanoparticlebased fluorescent bioimaging probes," Sci. Rep., vol. 3, pp. 1473–1479, 2013.
- [38] B. B. Campos, et al., "Carbon dots coated with vitamin B12 as selective ratiometric nanosensor for phenolic carbofuran," Sensors Actuators, B Chem., vol. 239, pp. 553– 561, 2017.
- [39] A. Nevin, et al., "Time-resolved photoluminescence spectroscopy and imaging: new approaches to the analysis of cultural heritage and its degradation," Sensors, vol. 14, no. 4, pp. 6338–6355, 2014.