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Photoluminescence Properties of Poly (Ethylene Glycol) Passivated Carbon Dots from Cassava Peels

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ABSTRACT

Carbon dots (C-dots) is a new type of luminescense nanoparticles that can be synthesized easily from natural sources, such as cassava peels. C-dots has been synthesized from cassava peels based green synthesis using low temperature. The surface of C-dots was passivated by poly(ethylene glycol) (PEG) with variations in volume from 0.5 ml, 1 ml, and 1.5 ml. Luminescense properties before and after passivasive with PEG characterized using photoluminescense (PL) and time resolved photoluminescence (TRPL) spectrophotometer. Peak wavelength spectrum of PL shows a red shift when 0.5 ml PEG was added. However, when the addition of PEG increases, peak wavelength spectrum of PL shows a blue shift. PL intensity decreased along with increasing of PEG volume. PL intensity influenced C-dots electron time decay linearly. C-dots electron time decay increased along with decreased of PL intensity. This results assigned potency that C-dots in water solution can be applied as bioimaging and metal ion and salt biosensing. however, it needs extra optical measurements to support our discovery.

Keywords: cassava peels, C-dots, electron time decay, FL intensity, PEG

INTRODUCTION

Carbon dots (C-dots) have emerged recently as one of the most interesting discoveries in the search for new nanomaterials (Algarra et al., 2014; Yu, Nan, & Zeng, 2017; Putro et al., 2019a). C-dots was discovered accidentally in 2004 as one of the substances produced by the purification of single-walled carbon nanotubes (SWNT) nanomaterials (Pires et al., 2015; Xu et al., 2004). C-dots are the newest alternative to nanomaterials that have been found and show several advantages over other nanoparticles (Ngu et al., 2016). C-dots are nanoparticles that emit light or fluorescent, and are not toxic compared to similar alternatives such as quantum dots (Algarra et al., 2014).

The characteristics of C-dots are not like nanodiamonds (Ding et al., 2014), C-dots are materials that belong to the class of 0-dimensional nanoparticles that are photoluminescence (Sugiarti & Darmawan, 2015). C-dots below 10 nm have a framework of sp^2 hybridized carbon atoms, abundant oxygen residues (Fang et al., 2012) and the surface is coated with groups of oxygen, polymers, or other species (Bao et al., 2015; Smagulova et al., 2017; Strauss et al., 2014; Unnikrishnan et al., 2016). C-dots show characteristics of blue or green luminescence under UV radiation (Baruah et al., 2014).

Putro et al., Showed that C-dots made from cassava peel using the hydrothermal method and passivated using PEG. The addition of PEG can increase fluorescence C-dots, usually called enhanced fluorescence (Putro et al., 2019b). Interestingly, we found C-dots made from cassava peel using the microwave method

and passivated using PEG, had different fluorescence phenomena. This addition of PEG can reduce the fluorescence of C-dots, usually referred to as quenched fluorescence.

RESEARCH METHODS

Synthesis of C-dots

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 a cup and heated using a 450 watt microwave oven for 40 minutes so that the solution settled. The precipitate obtained was then added 30 ml of distilled water and stirred using a 260 rpm magnetic stirrer for 10 minutes so that the precipitate could be completely dispersed.

The solution obtained was then filtered using 40 mesh filter paper to separate carbon deposits and C-dots. Furthermore, the solution obtained from the filtration was centrifuged with 10000 rpm for 10 minutes to separate the remaining carbon deposits and agglomerated particles to obtain clear colloids. Scheme of synthesis and passivated of C-dots can be seen in **Figure 1.**

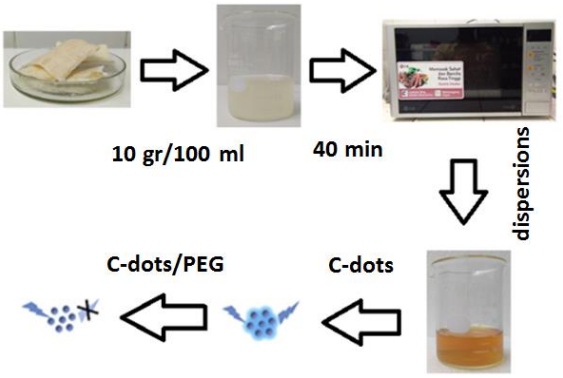

Figure 1. Scheme of synthesis and passivated of C-dots

Passivated of C-dots

The pasivasive process on the surface of C-dots was carried out by adopting the methods (Putro et al., 2019b). 0.2 ml of C-dots is heated at a temperature of 100^{o}C for 10 minutes so that the colloidal C-dots dried. Add PEG with a volume variation (0.5 ml, 1.0 ml, and 1.5 ml) and heated at temperature of 100^{o}C for 5 minutes. Add 10 ml of aquadest to disperse C-dots and PEG, respectively.

Characterization of C-dots/PEG

All samples were characterized by optical properties using a PL spectrophotometer with a 420 nm excitation source from a picosecond laser diode and produced a PL intensity spectrum. In addition, all samples were also characterized using a time resolved TRPL detector with excitation source from laser pulse and a 500 nm longpass filter to time electron decay C-dots.

RESULT AND DISCUSSION

PL is the emission or emission of light from an excited state in an electronic transition spontaneously after absorbing light. The PL process can basically be observed in the position of the spectrum, dynamics and efficiency to obtain relevant information. This spectrum informs about the energy difference between the excited state and the ground state which serves as the first indicator of material application (Kozák et al., 2016).

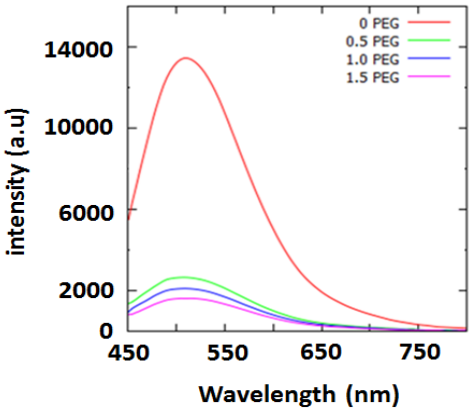

Figure 2. Photoluminescence spectra of colloidal C-dots

All types of C-dots have PL emissions at wavelengths independently of the excitation wavelength (Bao et al., 2015). The PL spectrum of colloidal C-dots

synthesized using the microwave method for 40 minutes and PEG-passivated can be seen in Figure 2. The peak of the maximum PL wavelength of colloid C-dots synthesized using the microwave method for 40 minutes and PEG passivated with a variation of 0.5 ml, 1.0 ml and 1.5 ml respectively were 507.98 nm, 509.82 nm, 508.90 nm and 503.85 nm, each with maximum PL intensity of 13734 au, 2742 au, 2176 au and 1731 au.

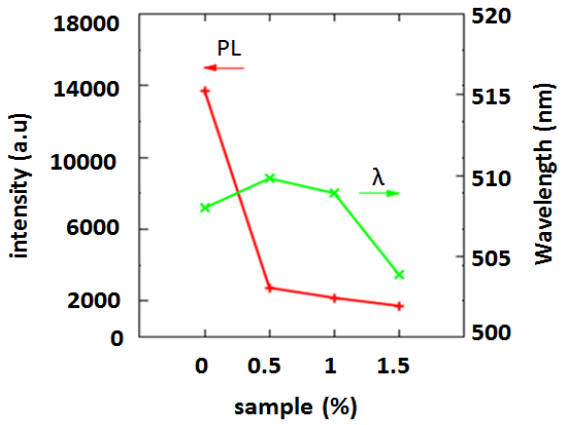

Figure 3. Curve relationship between peak PL intensity and wavelength of C-dots

The peak of the PL wavelength spectrum when adding 1 mg/ml of PEG shows redshift. But when the addition of PEG increases, the peak of the PL wavelength spectrum shows blue shift. PL intensity also decreased with increasing PEG volume. The relationship between peak intensity and maximum PL wavelength can be seen in Figure 3. 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, meaning the PL C-dots is not like quantum dots semiconductors. Surface oxidation serves as the center of exiton capture so as to produce PL that is related to surface conditions. Higher oxidation levels on the surface of C-dots suggest more surface defects (Ding et al., 2016). In addition, we suspect that the difference in PL C-dots intensity is due to its molecular density and content composition (Ding et al., 2016; Fatimah et al., 2017).

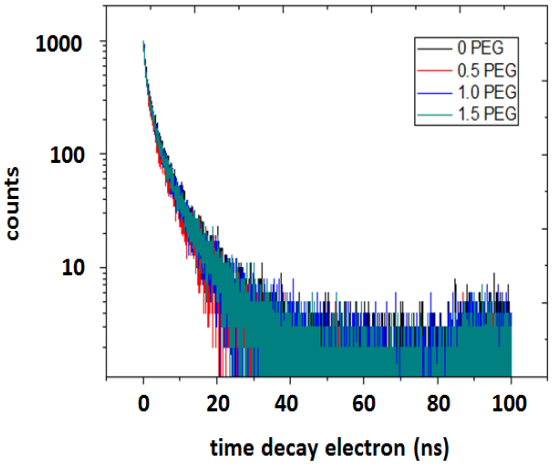

Figure 4. Time-resolved photoluminescence spectra of colloidal C-dots

Electron time decay is an important characteristic of light emitting nanoparticles. The difference in electron time decay corresponds to different electron-hole recombination mechanism (Zhang et al., 2013). Electron time decay measurement are used to determine the PL properties that show several energy levels (Jiang et al., 2018). Electron time decay measurement are carried out under the excitation pulse and decay is recorded after the excitation pulse finished (Kozák et al., 2016). Decay dynamics of C-dots can be analyzed by exponential multi decay models assuming a maximum of three discrete components (Nevin et al., 2014). The electron curve time of C-dots colloidal decay synthesized using the microwave method can be seen in Figure 4. The time of decay of C-dots electrons synthesized using the microwave method 40 minutes before being passivated and after PEG was passivated with a volume variation of 0.5 ml, 1.0 ml and 1.5 ml in a row were 3.743411 ns, 3.765122 ns, 4.178492 ns, and 4.247472 ns.

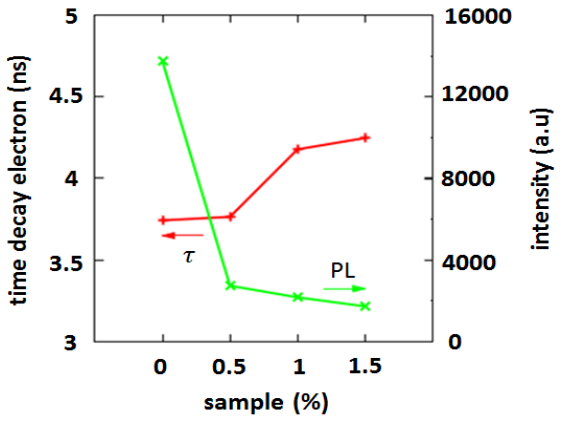

Figure 5. The relationship between PL intensity and Electron time decay C-dots

The position of the PL spectrum at maximum intensity and electron time decay on C-dots colloids is related to PL phenomenon events. The relationship between PL intensity and Electron time decay C-dots can be seen in Figure 5. PL intensity affects Electron time decay on colloidal C-dots. PL intensity decreased in each sample along with the length of Electron time decay on C-dots before being passivated and after PEG was invasive with variations in the volume of 0.5 ml, 1.0 ml and 1.5 ml, respectively. The short electron time decay can show that the electrons directly return to the valence band in pulsed laser excitation. Meanwhile, the longer electron time decay shows that there may be an additional energy level between the valence band and the conduction band. Short electron time decay shows high emission efficiency (Campos et al., 2017). In this case, C-dots which are PEG-passivated showed a longer time electron decay as the increase in PEG volume increased from 0.5 ml, 1.0 ml and 1.5 ml. In addition to PL intensity that can affect the time electron decay, changes in the functional groups of molecular binding (for example, breaking bonds) also affect emitters due to oxidation, aging and other modifications of organic molecules (Nevin et al., 2014).

CONCLUSION

C-dots were successfully used using PEG with volume variations of 0.5 ml, 1.0 ml and 1.5 ml. The addition of PEG volume variations can affect the peak wavelength and PL intensity, and the time of decay of electron C-dots. The peak of the PL wavelength spectrum when adding 1 mg / ml of PEG shows redshift. But when the addition of PEG increases, the peak of the PL wavelength spectrum shows blue shift. PL intensity also decreased with increasing PEG volume. C-dots that are passivated by PEG show a longer time of electron shedding as the increase in PEG volume increases. These results provide the potential for C-dots in aqueous solutions to be applied as bioimaging and biosensing metal ions and salts. However, additional optical measurements are needed to support our findings.

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REFERENCES

Algarra, M., Campos, B. B., Radotić, K., Mutavdžić, D., Bandosz, T., Jiménez-Jiménez, J., Rodriguez-Castellón, E., & Esteves da Silva, J. C. G. (2014). Luminescent carbon nanoparticles: Effects of chemical functionalization, and evaluation of Ag+ sensing properties. *Journal of Materials Chemistry A*, *2*(22), 8342–8351. https://doi.org/10.1039/c4ta00264d

Bao, L., Liu, C., Zhang, Z. L., & Pang, D. W. (2015). Photoluminescence-tunable carbon nanodots: Surface-state energy-gap tuning. *Advanced Materials*, *27*(10), 1663–1667. https://doi.org/10.1002/adma.201405070

Baruah, U., Gogoi, N., Konwar, A., Jyoti Deka, M., Chowdhury, D., & Majumdar, G. (2014). Carbon dot

based sensing of dopamine and ascorbic acid. *Journal of Nanoparticles*, 1–8. https://doi.org/10.1155/2014/178518

Campos, B. B., Contreras-Cáceres, R., Bandosz, T. J., Jiménez-Jiménez, J., Rodríguez-Castellón, E., da Silva, J. C. G. E., & Algarra, M. (2017). Carbon dots coated with vitamin B12 as selective ratiometric nanosensor for phenolic carbofuran. *Sensors and Actuators, B: Chemical*, *239*, 553–561. https://doi.org/10.1016/j.snb.2016.08.055

Ding, C., Zhu, A., & Tian, Y. (2014). Functional surface engineering of C-dots for fluorescent biosensing and in vivo bioimaging. *Accounts of Chemical Research*, *47*(1), 20–30. https://doi.org/10.1021/ar400023s

Ding, H., Yu, S. B., Wei, J. S., & Xiong, H. M. (2016). Full-color light-emitting carbon dots with a surface-state-controlled luminescence mechanism. *ACS Nano*, *10*(1), 484–491. https://doi.org/10.1021/acsnano.5b05406

Fang, Y., Guo, S., Li, D., Zhu, C., Ren, W., Dong, S., & Wang, E. (2012). Easy synthesis and imaging applications of cross-linked green fluorescent hollow carbon nanoparticles. *ACS Nano*, *6*(1), 400–409. https://doi.org/10.1021/nn2046373

Fatimah, S., Isnaeni, & Tahir, D. (2017). Sintesis dan karakterisasi fotoluminisens carbon dots berbahan dasar organik dan limbah organik. *POSITRON*, *VII*(2), 37–41. https://doi.org/10.26418/positron.v7i2.22660

Jiang, B. P., Yu, Y. X., Guo, X. L., Ding, Z. Y., Zhou, B., Liang, H., & Shen, X. C. (2018). White-emitting carbon dots with long alkyl-chain structure: Effective inhibition of aggregation caused quenching effect for label-free imaging of latent fingerprint. *Carbon*, *128*, 12–20. https://doi.org/10.1016/j.carbon.2017.11.070

Kozák, O., Sudolská, M., Pramanik, G., Cígler, P., Otyepka, M., & Zbořil, R. (2016). Photoluminescent carbon nanostructures. *Chemistry of Materials*, *28*(12), 4085–4128. https://doi.org/10.1021/acs.chemmater.6b01372

Nevin, A., Cesaratto, A., Bellei, S., D'Andrea, C., Toniolo, L., Valentini, G., & Comelli, D. (2014). Time-resolved photoluminescence spectroscopy and imaging: new approaches to the analysis of cultural heritage and its degradation. *Sensors*, *14*(4), 6338–6355. https://doi.org/10.3390/s140406338

Ngu, P. Z. Z., Chia, S. P. P., Fong, J. F. Y., & Ng, S. M. (2016). Synthesis of carbon nanoparticles from waste rice husk used for the optical sensing of metal ions. *New Carbon Materials*, *31*(2), 135–143. https://doi.org/10.1016/S1872-5805(16)60008-2

Pires, N. R., Santos, C. M. W., Sousa, R. R., de Paula, R. C. M., Cunha, P. L. R., & Feitosa, J. P. A. (2015). Novel and fast microwave-assisted synthesis of carbon quantum dots from raw cashew gum. *Journal of the Brazilian Chemical Society*, *26*(6), 1274–1282. https://doi.org/10.5935/0103-5053.20150094

Putro, P. A., Roza, L., & Isnaeni. (2019a). Karakterisasi sifat optik C-dots dari kulit luar singkong menggunakan teknik microwave. *Jurnal Teknologi Technoscientia*, *11(2)*, 128-136

Putro, P. A., Roza, L., & Isnaeni. (2019b).

The effect of poly (ethylene glycol) on the photoluminescence properties of carbon dots from cassava peels synthesized by hydrothermal methods. *SPEKTRA: Jurnal Fisika Dan Aplikasinya*, *4*(1), 11–20. https://doi.org/10.21009/SPEKTRA.041.02

Smagulova, S. A., Egorova, M. N., Tomskaya, A. E., & Kapitonov, A. N. (2017). Synthesis of carbon dots with tunable luminescence. *Journal of Material Sciences & Engineering*, *6*(5), 1–6. https://doi.org/10.4172/2169-0022.1000376

Strauss, V., Margraf, J. T., Dolle, C., Butz, B., Nacken, T. J., Walter, J., Bauer, W., Peukert, W., Spiecker, E., Clark, T., & Guldi, D. M. (2014). Carbon nanodots: Toward a comprehensive understanding of their photoluminescence. *Journal of the American Chemical Society*, *136*(49), 17308–17316. https://doi.org/10.1021/ja510183c

Sugiarti, S., & Darmawan, N. (2015). Synthesis of fluorescence carbon nanoparticles from ascorbic acid. *Indones. J. Chem*, *15*(2), 141–145.

Unnikrishnan, B., Wu, C. W., Chen, I. W. P., Chang, H. T., Lin, C. H., & Huang, C. C. (2016). Carbon dot-mediated synthesis of manganese oxide decorated graphene nanosheets for supercapacitor application. *ACS Sustainable Chemistry and Engineering*, *4*(6), 3008–3016. https://doi.org/10.1021/acssuschemeng.5b01700

Xu, X., Ray, R., Gu, Y., Ploehn, H. J., Gearheart, L., Raker, K., & Scrivens, W. A. (2004). Electrophoretic analysis and purification of fluorescent single-walled carbon nanotube fragments. *Journal of the American Chemical Society*, *126*(40), 12736–12737. https://doi.org/10.1021/ja040082h

Yu, J., Nan, J., & Zeng, H. (2017). Size control of nanoparticles by multiple-pulse laser ablation. *Applied Surface Science*, *402*, 330–335. https://doi.org/10.1016/j.apsusc.2017.01.094

Zhang, X., Zhang, Y., Wang, Y., Kalytchuk, S., Kershaw, S. V., Wang, Y., Wang, P., Zhang, T., Zhao, Y., Zhang, H., Cui, T., Wang, Y., Zhao, J., Yu, W. W., & Rogach, A. L. (2013). Color-switchable electroluminescence of carbon dot light-emitting diodes. *ACS Nano*, *7*(12), 11234–11241. https://doi.org/10.1021/nn405017q