Concentration effect on optical properties of CDots composite film from sugar (sucrose)

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Abstract. Carbon dots (CDots) are one of the fascinated carbon-based nanomaterials which have broad applications. One fields that rarely been explored is using CDots as a composite luminescence film with addition of polyvinyl alcohol (PVA). The luminescence properties of CDots is a great potential that can be used to make luminescence PVA/CDots films since CDots are known as materials that have strong luminescence. This study aims to determine the effect of CDots concentration on the optical properties of CDots/PVA composite. We also observed the effect of excitation wavelengths to emission of CDots/PVA composite. The carbon dots was synthesized from commercial sugar using microwave technique. UV-Vis spectroscopy characterization showed that the concentration of CDots affect to surface state of CDots. Surface energy bands from individual CDots may overlap one to another creating new energy level, so that the absorbance peak experiences red shift. Photoluminescence spectra results showed that the excitation wavelength caused a difference in the emission wavelength in the sample. Excitation with a blue laser produces green emissions while excitation with a green laser produces red emissions. The results show that the synthesized CDots have potential to be used as luminescence films. The as-synthesized CDots shows great luminescence properties and can be varied with several controlled parameters.

1. Introduction

Indonesia is classified as one of the tropical countries overgrown with various plants, one of them is sugar cane. Cane (Saccharum officinarum) is the basic ingredient for making sugar that is consumed by many Indonesian people. In addition to consumption, sugar can also be used as a basis for the synthesis of carbon nanodots (CDots) [1-3]. Granulated sugar is used as the basis for making CDots because it is easily found especially in Indonesia, the price is relatively cheap, and has a carbon content which is the main constituent in CDots.

CDots are a new class of dimensionless carbon nanomaterials that are less than 10 nm [3]. Carbon dots are different from other carbon-based materials because they have strong photoluminescence and have an easy synthesis process [4]. Photoluminescence on CDots can originate from quantum confinement effects and surface states. Emissions from state surfaces usually have a narrower band gap. Therefore the result of emission has a longer wavelength compared to the emission originating from the quantum confinement effect [5,6]. In general, CDots consist of elements that are abundant in nature and free of heavy metals. Various advantages possessed by CDots make this
material interesting to study including having luminescence with various colors, non-toxic, and the stability of optical properties [7]. With these properties, Cdots can be used in various applications such as bioimaging [8,9], optical devices [3], photocatalysis [10], medical diagnostics [11], and nanosensors [12,13].

The basic ingredients of making Cdots can come from chemicals and natural ingredients. Natural ingredients for making Cdots can come from fruit skins, egg shells, household waste, leaves, seeds, and sugar [4,14]. When the precursors have been synthesized into Cdots there is no significant difference between the two. Thus, in this study used natural ingredients, sugar which are more eco-friendly [15].

In general, Cdots synthesis can be done in two ways, the top-down method that breaks large particles into nanometer sizes and the bottom-up method that starts from atoms or molecules collected to form the desired nanometer-sized particles [16]. Some methods used in the synthesis of Cdots are the hydrothermal method [17,18], the electrochemical method [19], and the microwave method [2,20,21]. In this study the microwave method is used because this method classified eco-friendly, green synthesis, economical, and the resulting luminescent colors are stronger [8]. Another advantage of the microwave method is that the time required is shorter in minutes than the hydrothermal method which takes several hours. Heating from microwaves is also more uniform, thereby reducing the possibility of other reactions that are not desired [22]. With the microwave method, Cdots are then mixed with polyvinyl alcohol (PVA) into PVA / Cdots films. PVA / Cdots are used as films because they are hydrophilic and transparent which serve to minimize the barriers to excitation and emissions from Cdots [23].

Composite films affect the optical properties of Cdots where the fluorescence emissions from Cdots are related to composite films [24]. Composite films have several advantages such as having excellent biocompatibility, having a good photoluminescence response [25], and having an easy to use surface such as in biosensing, bioimaging, and biooptics [26]. Some recent research used PVA/Cdots composite films as security label to anti-counterfeiting at the company level [27] and applied to encrypt data [28]. By using the strong luminescence properties of Cdots and PVA that are transparent and easily processed, this PVA/Cdots composite film is a promising material to be applied into securities. In addition, [29] also uses PVA/Cdots composite film to dye removal because it has high and stable adsorption levels of Cdots in atmospheric conditions. Liu et al., used PVA/Cdots composite films for electrode modification on sensors coupled with Ru(bpy)$_3^{2+}$ because of the sensitivity of a good combination for sensor based [30].

However, the applications that have been in the most recent research still using chemicals as a Cdots precursor. Problems arising from previous studies also concerning luminescence resulting from suboptimal Cdots [31] and luminescence from PVA/Cdots can be accessed well at annealing temperatures of 200 °C [28]. Therefore in this paper Cdots are used sugar as natural precursors, which are easily found and low cost process. To find out how the luminescence produced by PVA/Cdots films, this paper discusses the variation of Cdots concentration on the wavelength of emissions. UV-Vis characterization was performed to determine the effect of concentration on Cdots through the absorbance of the sample. Characterization of photoluminescence was carried out to determine the wavelength of emissions from Cdots.

2. Experimental Method
Cdots are made of basic ingredients of sugar that are sold in the market and then synthesized using microwave techniques. 15 grams of commercial sugar are dissolved in 100 mL of water using a magnetic stirrer. The sugar solution was then placed in a microwave set at 450 Watt for 40 minutes so the sugar solution becomes a dark brown dry caramel. After that, the sugar crust was dissolved in 100 mL of water and centrifuged to separate colloid Cdots from the residue. In this study, two variations of Cdots concentration were used. PVA / Cdots composite solutions were prepared by dissolving 4 grams of PVA at 200 mL of distilled water using a hot plate magnetic stirrer. After that 2 mL Cdots were mixed with 28 mL of PVA solution using an ultrasound cleaner. After that, the PVA / Cdots
solution is dropped cast onto a baking sheet and heated in an oven until a PVA / CDots composite layer is formed. The characterization carried out in this research is the UV-Vis spectroscopy test to determine the absorbance of the sample and the photoluminescence test to determine the wavelength of emissions from the sample.

3. Result and Discussion

Carbon dots were successfully made by the microwave method. The formation of CDots is marked by the appearance of green in the sample when irradiated by a 405 nm UV laser as shown in Figure 1.

![Figure 1. Process of irradiating sample using a 405 nm uv laser (a) light without laser (b) light with laser (c) dark with laser without filter (d) dark with laser and 500 nm long pass filter.](image)

The results of UV-Vis characterization showed that there were two peaks of absorbance at low concentrations but there were three peaks at high concentration CDots. The peaks at high concentrations are at wavelengths of 267 nm, 305 nm, and 395 nm for CDots solution. In the PVA / CDots solution the observed peak is at a wavelength of 265 nm. For low concentrations, we obtained peaks at wavelengths of 297 nm and 341 nm for CDots solution. In the PVA / CDots solution we obtained peaks at wavelengths of 262 nm and 385 nm. The first absorbance peak shows the $\sigma \rightarrow \sigma^*$ energy transition where the $\sigma \rightarrow \sigma^*$ transition shows the C-H bond [1]. The second peak shows the $\pi \rightarrow \pi^*$ energy transition where the $\pi \rightarrow \pi^*$ transition indicates the C = C bond [32,23]. The third peak is the $n \rightarrow \pi^*$ energy transition from a state where the $n \rightarrow \pi^*$ transition indicates the C = O bond [32-36]. $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions are transitions originated from core carbon dots while $n \rightarrow \pi^*$ transitions are transitions originated from surface state carbon dots [1,16].

CDots concentration affects the shift in absorbance peak wavelength. Based on Table 1. CDots with high concentration experiences smaller shifts (38 nm) compared to CDots with low concentrations (44 nm). Likewise, the absorbance peak wavelength in the PVA / CDots solution with high concentration of CDots solution is smaller (81 nm) compared to the that of low concentration CDots solution (123 nm). From Table 1 it is found that the absorbance peak shift in the PVA / CDots is more significant compared to the CDots solution only.

The addition of PVA to the CDots solution causes a reduction in the initial concentration of CDots. The reduced concentration of CDots causes a shift in the absorbance peak wavelength as confirmed in Figure 2. In Figure 2 it is obtained that the resulting absorbance graph shifts to the left for both concentrations. This is influenced by the concentration of CDots, where when the concentration of CDots in the solution gets lower then the graph will shift to the shorter wavelength. The shift in the graph is also influenced by the energy overlapping of the CDots so that new energy levels appear that cause a shift in the emission wavelength [1].
Figure 2. UV-Vis spectra of samples at various concentration (a) high concentration (b) low concentration.

Table 1. Absorbance peak wavelength of UV-Vis characterization.

| Concentration | Wavelength (nm) | CDots | PVA/CDots |
|---------------|----------------|-------|-----------|
|               | Peak 1 | Peak 2 | Peak 3     | Peak 1 | Peak 2 | Peak 3 |
| High          | 267    | 305    | 395       | 265    | 346    | -      |
| Low           | 297    | 341    | -         | 262    | 385    | -      |

Figure 3. Photoluminescence spectra of samples at various concentrations.
Table 2. Emission peak wavelength of photoluminescence characterization.

| Concentration | Wavelength (nm) | Blue laser excitation | Green laser excitation |
|---------------|-----------------|------------------------|------------------------|
|               | CDots solution  | PVA/CDots solution     | PVA/CDots film         | CDots solution | PVA/CDots solution | PVA/CDots film     |
| High          | 567             | 520                    | 550                    | 639             | 638             | 614             |
| Low           | 554             | 555                    | 529                    | 626             | 623             | 622             |

The results of the photoluminescence of the sample are shown in Figure 3. In samples with high concentrations that are excited by the blue laser the peak wavelengths are at 567 nm for CDots solution, 520 nm for PVA / CDots solution, and 550 nm for PVA / CDots composite layers. Low concentration samples which were excited by blue laser produced a peak wavelength at 554 nm for CDots solution, 555 nm for PVA / CDots solution, and 529 nm for PVA / CDots composite layers. Samples with high concentrations which were excited by green laser produced wavelength peaks at 639 nm for CDots solution, 638 nm for PVA / CDots solution, and 614 nm for PVA / CDots composite layers. Samples with low concentrations that are excited by green lasers produce peak wavelengths at 626 nm for CDots solution, 623 nm for PVA / CDots solution, and 622 nm for PVA / CDots composite layers.

There is a difference between the results of the emissions in the solution and the coating in the samples. When the PVA / CDots solution is formed into a layer, the peak wavelength emission shifts to the left. The formation of the solution into a composite layer causes the loss of solvents from CDots which causes the graph to shift to the left as confirmed in Figure 3 [3]. High concentrations caused peak shifts that are more significant than low concentrations as shown in Figure 3.

Conclusion
Carbon dots solution made from sugar and composite film from PVA/CDots were successfully synthesized using microwave technique. Concentration affects the optical properties of CDots. The lower concentration of CDots with the addition of polyvinyl alcohol causes the peak wavelength to be greater or the graph will red shift. Lighting excitation affects CDots emissions. Excitation of lighting with a blue laser causes the luminescent produced to be in the range of wavelengths that are green. Excitation of lighting with a green laser causes the luminescent produced to be in the range of red wavelengths. The green color of the light is confirmed by the results of the photoluminescence test with a blue laser. Based on Figures 3a and 3b, the resulting CDot luminescence is at a peak of 520 nm - 564 nm where this wavelength range is green. The red color of the light is confirmed from the results of the photoluminescence test with a green laser shown in Figure 3c, d. The luminescence that appears at the peak of 614 nm - 639 nm where this wavelength range is red.

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References

[1] Isnaeni, Herbani Y and Suliyanti M M 2018 J. Lumi. 198 pp.215-9
[2] Ansi V A and Renuka N K 2018 Sens. Actuators B:Chem. 264 pp.67-75
[3] Joseph J and Anappara A A 2017 Phys. Chem. Chem. Phys. 19(23) pp.15137-44
[4] Isnaeni, ddZufara B S, Lewa I W L, Herbani Y and Shiddiq M 2020 Advances in Natural Sciences: Nanoscience and Nanotechnology 11(1) p.015003
[5] Liu Z, Zou H, Wang N, Yang T, Peng Z, Wang J, Li N and Huang C 2018 Sci. China Chem. 61(4) pp.490-6
[6] Zhu S, Song Y, Wang J, Wan H, Zhang Y, Ning Y and Yang B 2017 Nano Today 13 pp.10-14
[7] Das R, Bandyopadhyay R and Pramanik P 2018 Materials today chemistry 8 pp. 96-109
[8] Bhattacharya S, Phatake R S, Barnea S N, Zerby N, Zhu J J, Shikler R, Lemcoff N G and Jelinek R 2019 ACS nano13(2) pp.1433-42
[9] Lan M, Zhao S, Zhang Z, Yan L, Guo L, Niu G, Zhang J, Zhao J, Zhang H, Wang P and Zhu G 2017 Nano res. 10(9) pp.3113-23
[10] Yu H, Shi R, Zhao Y, Waterhouse G I, Wu L Z, Tung C H and Zhang T 2016 Adv.Mater. 28(43) pp.9454-77
[11] Miao X, Yan X, Qu D, Li D, Tao F F and Sun Z 2017 ACS Appl. Mater. Interfaces 9(22) pp.18549-56
[12] Gong X, Lu W, Liu Y, Li Z, Shuang S, Dong C and Choi M M 2015 J. Mater. Chem.B3(33) pp.6813-9
[13] Gong X, Lu W, Paau M C, Hu Q, Wu X, Shuang S, Dong C and Choi M M 2015 Anal. Chim. Acta 861 pp.74-84
[14] Zuo P, Lu X, Sun Z, Guo Y and He H 2016 Microchim. Acta 183(2) pp 519-42
[15] Yuan F et al 2020 Nature Photon. 14(3) pp.171-6
[16] Dwandaru W S B, Bilqis S M and Wisnuwijaya R I 2019 Mater. Res.Express 6(10) p.105041
[17] Papaioannou N, Marinovic A, Yoshizawa N, Goode A E, Fay M, Khlobystov A, Titirici M M and Sapelkin A 2018 Sci. Rep. 8(1) pp. 1-10
[18] Zheng X, Ding G, Wang H, Cui G and Zhang P 2019 Mater. Lett. 238 pp.22-25
[19] Lin Y S, Lin Y, Periasamy A P, Cang J and Chang H T 2019 Nanoscale Advances 1(7) pp.2553-61
[20] Zhao C, Li X, Cheng C and Yang Y 2019 Microchemical J. 147 pp.183-190
[21] Rahmawati I, Intan R and Zakaria M 2018 J. Phys.: Conf. Ser. 985(1) p. 012004 IOP Publishing
[22] De Medeiros T V, Manioudakis J, Noun F, Macairan J R, Victoria F and Naccache R 2019 J. Mater. Chem.C7(24) pp.7175-95
[23] Kwan M N H, Leo C P, Senanayake S A, Lim G K and Tan M K 2019 J. Environ. Chem. Eng. p.103187
[24] Shauloff N, Bhattacharya S and Jelinek R 2019 Carbon152 pp.363-71
[25] Liu Y, Li W, Wu P, Ma C, Wu X., Xu M, Luo S, Xu Z and Liu S 2019 Sens. Actuators B:Chem. 281 pp. 34-43
[26] Solhi E and Hasanzadeh M 2019 TrAC Trends in Analytical Chemistry
[27] He J, He Y., Chen Y, Zhang X, Hu C, Zhuang J, Lei B and Liu Y 2018 Chem. Eng. J. 347 pp.505-13
[28] Tian Z, Li D, Ushakova E V, Maslov V G, Zhou D, Jing P, Shen D, Qu S and Rogach A L 2018 Adv. Sci. 5(9) p.1800795
[29] El-Shamy A G and Zayied H S S 2020 Synth. Met. 259 p.116218
[30] Liu Z, Zhang X, Cui L, Wang K and Zhan H 2017 Sens. Actuators B:Chem. 248 pp.402-10
[31] Kwan M N H, Leo C P, Senanayake S A, Lim G K and Tan M K 2020 J. Environ. Chem. Eng.8(3) p.103187
[32] Mazrad Z A I, Kang E B, In I and Park S Y 2018 Luminescence33(1) pp. 40-46
[33] Fatimah S, Isnaeni I and Tahir D 2017 POSITRON7(2) pp.37-41
[34] Jhonsi M A and Kathiravan A 2017 J. Lumin.192 pp.321-7
[35] Putro P A, Roza L and Isnaeni I J. Phys.: Theor. Appl.2(2) pp.43-52
[36] Li Q, Zhou M, Yang M, Yang Q, Zhang Z and Shi J 2018 Nat. Commun.9(1) pp.1-8