Synthesis of fluorescent composite films PVA/CDots from orange concentrate with microwave technique

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Abstract. Carbon dots (CDots) is one of the fluorescent materials that can be made of organic materials. CDots materials can be obtained easily using organic materials that have carbon chain. Synthesis of CDots with orange concentrate as a PVA/CDots composite film using microwave was carried out and the optical properties of synthesized CDots with various concentrations of orange concentrate were observed using emission of CDots. The successful synthesis of CDots could be recognized by simply irradiating a 405 nm UV laser into a sample and then further characterization using a UV-Vis spectrophotometer and photoluminescence. The results of UV-Vis characterization showed the effect of concentration variation on the absorbance peak wavelength. For high concentration, the absorbance peak wavelength is longer than that of low concentration. This is due to the surface state CDots. The characterization of photoluminescence shows CDots emissions. Excitation using a blue laser (λ=420 nm) produces emission peaks that are in the range of green wavelengths, whereas excitation using green laser (λ=532 nm) produces emission peaks that are in the range of yellow-red wavelengths. The results of the synthesized PVA/CDots films from orange concentrates have good potential to be applied as glowing packaging.

1. Introduction
Fluorescent materials have great influence on applications in the fields of bio imaging, LED, and photocatalysis [1]. Fluorescent materials can be made of inorganic or organic materials. Carbon Dots (CDots) is a fluorescent material that can be synthesized from various carbon sources and can be made of organic ingredients [2]. Example of the organic materials, which are often made into CDots, are from plants, such as ipomoea aquatica [3], ocimum sanctum [4], ginkgo fruits [5], dragon fruit and pear [6], orange fruit [7] and many other organic materials.

CDots synthesis is mostly done easily using organic materials to replace Quantum Dots which are usually made using inorganic material because they have some advantages. The advantages of CDots are cheap, non-toxic [8], low toxicity, good biocompatibility [9], easy synthesis, production of fluorescence on UV exposure [10], and several other advantages. These advantages make CDots can be widely applied in various fields, including anti-counterfeiting applications printed on a banknote and a merchandise tag [11], amino acid sensors [12], fluorescent plastics manufacturing and...
fingerprints imaging [13], detection of Hg2+ ions [14], and has potential in various biomedical applications [15].

CDots synthesis method can be done with top-down or bottom-up techniques, method selection CDots synthesis will affect the process conditions, quantum yield, and uniformity of the CDots [16]. The microwave method is one of the bottom-up methods that have been chosen in CDots synthesis because it has advantages like cheap, simple, easy [17], lower instances side reactions and fewer byproduct formation, and quicker reaction [18]. The quicker reaction using the microwave method can reduce heating time compared to the method conventional [19]. Also, carbon-based materials have a strong tendency to interact with microwaves, which makes it possible to achieve efficient and localized heating thus supporting the carbonization processes and facilitate the emergence of distinct morphology of the nanostructures [20].

Nanoparticles that are currently developing can be used as composite materials on polymers, one of which is Carbon Dots [21]. Polymer nanocomposites have attracted the attention of many research groups because of their unique physicochemical properties and wide applications [22]. In fact, among all the polymeric materials, PVA (Polyvinyl acetate, PVA or PVAc) is recently rated as one of the most important polymers because it’s a simple fabrication, stability against atmospheric conditions, affordability, visibility, and others [23]. In previous research, synthesized PVA/CDots composite films have been successfully done. Jiang et al [24] synthesized PVA/CDots composite film, in which m-phenylenediamine citric acid was used as carbon sources for advanced anti-counterfeiting. Also, Kwan et al [25] synthesized PVA/CDots composite film from citric acid and synthesized using microwave-assisted method. Therefore, considering the result of the research [24,25], it provokes the idea for synthesized PVA/Cdots composite film with CDots produced from orange concentrate can be used for the advanced glowing packaging. The uses of PVA for composites in the synthesis of CDots for research are to minimize hindrances to the excitation and CDots emissions [25]. The synthesis of CDots in this study was carried out by the microwave method which aims to determine the optical properties of CDots with variations in the concentration of orange concentrates and variations of excitation wavelength to determine the emission CDots.

2. Experimental
In this study three types of samples were made, the CDots solution, PVA/CDots solution, and PVA/CDots film. The synthesis of the CDots solution was done by the microwave method. Orange concentrate as a basic ingredient in making CDots obtained from pulpy orange beverage. Orange concentrate as much as 20 ml for each high concentration samples and low concentration samples are heated in microwave 450 W for 10 minutes. Then the samples are dissolved in purified water with hot stirrer 300 rpm for 10 minutes and centrifuged to separate the CDots solution with the precipitate. The manufacture of PVA/CDots solution was done by mixing the PVA solution with CDots solution. 28 ml PVA solution and 2 ml CDots solution was stirred using an ultrasonic bath for 15 minutes. PVA/CDots coating is made with 5 ml of PVA/CDots solution which is oven-shaped (baking pan) for 1 hour 45 minutes at a temperature of around 54°C so that the PVA/CDots film is obtained in the form of a brownish yellow transparent plastic. To find out the success of CDots synthesis, the samples were simply confirmed by irradiating a 405 nm UV laser into samples. Furthermore, we characterized samples using UV-Vis spectrophotometer and Photoluminescence (PL). UV-Vis spectrophotometer characterization was performed to determine the CDots absorbance, while PL characterization was performed to determine the wavelength of CDots emissions seen from the formation of the CDots luminescence spectrum. PL characterization is done by irradiating a green laser (\(\lambda = 532\) nm) and a blue laser (\(\lambda = 420\) nm) to the sample.

3. Result and discussion
The results of the synthesis of CDots based on orange concentrate is brown for CDots solution samples, yellowish for PVA/CDots solution samples, and transparent brownish-yellow for PVA/CDots film samples. The test results by irradiation of a 405 nm UV laser into the samples are shown in figure
1. The successful synthesis of CDots with orange concentrates shows green glow (figure 1 (c)). This indicates that the results of the synthesis of CDots are based orange concentrate has good fluorescence properties.

![Figure 1](image)

**Figure 1.** The test results by irradiation of a 405 nm UV laser into the sample (a) light without a laser (b) dark with laser without filter (c) dark with laser and 500 nm long-pass filter.

UV-Vis characterization was performed to determine absorbance patterns at certain wavelengths which are displayed as curve between absorbance (x axis) and wavelength (nm) in y-axis. Results of UV-Vis characterization for high concentrations and low concentrations is shown in figure 2.

![Figure 2](image)

**Figure 2.** (a) UV-Vis spectra at high concentration, and (b) low concentration of samples.

The results of characterization for high concentrations in CDots solution showed 3 absorbance peaks, which are at 265 nm, 302 nm, and 399 nm. While the PVA/CDots solution showed 2 peaks the absorbance at 256 nm, and 308 nm. Then, the characterization results for low concentrations at CDots solution showed 3 peaks of absorbance, at 253 nm, 304 nm, and 404 nm. While the PVA/CDots solution showed 2 peaks of absorbance at 252 nm and 292 nm. The first peak at that wavelength showed the electron transition $\pi \to \pi^*$ (core) and second, and third peak indicates the electron transition $n \to \pi^*$ (surface state). Transition $\pi$ (bonding) to $\pi^*$ (antibonding) shows the core transition of CDots, which is $C = C$, while the transition of $n$ (nonbonding) to $\pi^*$ (antibonding) shows the surface transition of CDots to atoms other than atom C. This is following previous reports by Anwar et al [20].
Table 1. The absorbance peak wavelength of UV-Vis characterization.

| Concentration | Wavelength (nm) |
|---------------|-----------------|
|               | CDots solution  | PVA/CDots solution |
|               | Peak 1 | Peak 2 | Peak 1 | Peak 2 | Peak 3 |
| High          | 265    | 308    | 265    | 302    | 399    |
| Low           | 252    | 292    | 253    | 304    | 404    |

Based on the two charts the test results, it can be seen that the microwave method was successfully used to synthesize CDots. This is indicated by the peak absorbance in the solution CDots, which are in the wavelength range of 250-310 nm. This is consistent with the results of previous studies, which showed that CDots had absorbance spectra in the UV region with the tail extending to the visible region [26]. The addition of PVA in the CDots solution was aimed to form PVA/CDots composite films. When PVA is added, a long shift occurs to longer wavelength, which is as much as 91 nm (from 308 nm to 399 nm) for high concentration, and as much as 112 nm (from 292 nm to 404 nm) for low concentrations. Addition PVA in CDots solution with variations in concentration shows that the higher the concentration, then the absorbance peak of the CDots shifts to the shorter wavelength, wherein the spectrum, a long shift occurs for 5 nm (from 404 nm to 399 nm), while in CDots solution with variations in concentration shows that the higher the concentration, then the absorbance peak of the CDots shifts to the right, wherein the spectrum, a long shift occurs wavelength of 16 nm (from 292 nm to 308 nm). The most dominant absorbance peak depends due to variations in concentration that is on the surface state with transitions n → π *.

Table 2. The emission peak wavelength of PL characterization with a blue laser (λ=420 nm)

| Concentration | Wavelength (nm) |
|---------------|-----------------|
|               | CDots solution  | PVA/CDots solution | PVA/CDots film |
| High          | 532             | 525                | 502            |
| Low           | 535             | 523                | 504            |
PL characterization was carried out to determine the maximum emission wavelength produced by CDots. PL characterization is related to the transition from excited to ground state. The results of PL characterization with blue and green lasers are shown in figures 3 and 4. In this spectrum, the physical meaning of intensity is the bright dim luminescence of CDots and physical meaning of the wavelengths is the color of luminescence. The peak emission intensity is the result of PL characterization strengthen the indication of the formation of CDots in the sample due to oven or microwave heating. The appearance of luminescence is one of the properties of CDots [27].

**Table 3.** The emission peak wavelength of PL characterization with green laser (λ=532 nm).

| Concentration | Wavelength (nm) | CDots solution | PVA/CDots solution | PVA/CDots film |
|---------------|-----------------|----------------|-------------------|----------------|
|               | Peak 1 | Peak 2 | Peak 1 | Peak 2 | Peak 1 |
| High          | 598    | -     | 623    | -     | 633   |
| Low           | 592    | -     | 577    | 635   | 600   |

The heating produces more CDots that absorbs more excitation energy. Excited electrons of CDots is an unstable state, so the electrons return to the ground state. This transition is done by radiating electromagnetic waves at certain wavelengths. This emission is detected as intensity emissions from CDots on PL characterization charts [28].

Figures 3 and 4 show that the intensity of the PL spectrum is also affected by variations in concentration. The intensity value of the PVA/CDots film tested using a blue laser for high concentrations was 985.68 a.u. and for low concentrations 406.27 a.u (Figure 3). Then, the intensity value of the PVA/CDots film tested using a high concentration green laser was 94.75 a.u. and for low concentrations 73.62 a.u (Figure 4). Based on the intensity value, it can be seen that the greater the sample concentration, then the higher the intensity value. The higher the intensity value indicates that the number of CDots produced is increasing [29].
Figure 4. (a) PL spectra with a green laser (\(\lambda=532\) nm) at high concentration, and (b) low concentration of sample.

The characterization results for blue laser excitation at high concentrations and low concentrations indicate peak emissions which are in the wavelength range of green color is 495-570 nm so it can be concluded that the synthesized CDots produced a green glow. This also applies to the results of the test after being exposed to a UV 405 nm laser that is tinted green (figure 1). Then, for green laser excitation at high concentrations and low concentrations shows emission peaks are in the range of the yellow-red wavelength, which is 570-750 nm. The difference of wavelength range of peak emissions produced by the blue laser and green laser excitation is because there is a difference in the energy absorbed by electrons in carbon dots due to different excitation lasers.

4. Conclusion

Synthesis of CDots with orange concentrate as a PVA/CDots composite film has been successfully carried out using the microwave technique. UV-Vis characterization shows that the concentration can affect the optical properties of the CDots. Higher the concentration of CDots resulted peak shift to longer wavelength or the spectrum will shift to the right, and vice versa. The PL characterization showed that the concentration affected the intensity and the wavelength of the excitation affected the emission of CDots. The greater the sample concentration, then the higher the intensity value. Excitation wavelength affects the emissions of CDots. Excitation lighting with a blue laser (\(\lambda=420\) nm) produces luminescence or peak emissions that are at the wavelength range is green, while the lighting is excited by a green laser (\(\lambda=532\) nm) produces luminescence or peak emissions that are in the range of colored wavelength yellow-red. The results of the synthesized PVA/CDots films from orange concentrates have good potential to be applied as glowing packaging.

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