CDOTS AND CDOTS/S SYNTHESIS FROM NAM-NAM FRUIT (*CYNOMETRA CAULIFLORA L.*) VIA FRYING METHOD USING COOKING OIL

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This research aims to synthesis carbon-dots (Cdots) and carbon dots/sulphur (Cdots/S) from nam-nam fruit via oil based frying method and to characterize the samples using UV-Vis spectroscopy, PL, XRD, and TRPL. The UV-Vis result upon the Cdots sample shows absorbance peaks at 242 nm and 268 nm, whereas Cdots/S sample shows absorbance peaks at 228 nm and 268 nm. The PL characterization shows green luminescence with peak intensities at 497.87 nm and 498.79 nm for Cdots and Cdot/S, respectively. TRPL results show the electrons decay lifetime duration of Cdots and Cdots/S, i.e.: 2.46 ns and 1.71 ns, respectively.

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Keywords: Cdots, Cdots/S, Nam-nam fruit, Cooking oil, Frying method

1. Introduction

The development of nanotechnology is very rapid. Nanotechnology is one important area in modern research relating to the design, synthesis, and engineering of materials in the scale of 1 nm to 100 nm [1]. Nanotechnology is rapidly developing by producing nanoparticles having unique and remarkable physical and chemical properties related to their sizes. Unlike bulk material, the characteristics of nanomaterials are based on their size, shape, and surface morphology [2]. One exciting development in nanotechnology is the research in carbon-dots (Cdots) material. Previous study [3] shows that Cdots have good solubility, non-toxic, and have excellent luminescence. Cdots may be utilized for many applications, such as bio-imaging, sensors, drug delivery, catalysts, and photovoltaic devices [4]. The abundant raw materials that exist in nature ignite a lot of Cdots studies based on various materials such as ginger and galangal herb [5], simple oil-based heating [6], tomatoes [7], and coffee [8]. One method to synthesize Cdots, which is simple and easy to be conducted, is oil-based frying method. In addition, the advantage of this bottom-up method is that it does not need sophisticated tools and do not require harmful chemicals. Many studies have been conducted to produce Cdots via the frying method, one of which is using cooking oil wastes [9].

Nam-nam (*Cynometra cauliflora L.*) is a species of plant that is found in the South East Asia region. Nam-nam fruit contains triterpenoid, flavonoid, and saponin compounds [10]. Based on a previous study [11], methanol extract of nam-nam leaf has phenolic content and has antioxidant activity. However, this plant has been forgotten so that it becomes quite rare. Therefore, there is an urgent need to cultivate this plant because the various benefits mentioned. One way to motivate in cultivating nam-nam plant is by showing a benefit of it, i.e.: using the fruit part as a precursor in the synthesis of Cdots.

Moreover, we also modify the Cdots by adding sulphur as an impurity. The addition of sulphur to Cdots (Cdots/S) produces a cross-linker in the Cdots, which reduces the UV-Vis absorbance and affects the lower band gap of the Cdots. Furthermore, the amount of Cdots/S can change the physical properties of the Cdots. It is also expected that the solutions when irradiated by UV light produce luminescence colors, which can be useful in various fields.

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2. Experimental

The materials used in this study are i) nam-nam fruit, ii) distilled water, iii) cooking oil (Filma brand), iv) n-hexane (C_6H_{14}) solution, and v) sulphur powder. The tools used in this study are i) a frying pan, ii) an oven, iii) a pipette, iv) beaker glasses, v) aluminium foils, vi) a stopwatch, vii) plastics, viii) filter papers, ix) a digital scale, and x) a heater.

a) b) c) d)

Fig. 1. Pre-cursor material for Cdots synthesis, i.e.: nam-nam fruit tree (a), nam-nam fruits (b), nam-nam fruits that have been crushed, and the synthesis of nam-nam fruits by frying method.

The steps of synthesizing Cdots from nam-nam fruit via a frying method are given as follo ws: i) open and take the meat of the nam-nam fruit, ii) cut small pieces of namnam fruit meat using a knife, iii) pound the nam-nam fruit meat until it is smooth, iv) pour 250 ml of cooking oil into a f rying pan and heat the frying pan with medium heat, v) pour the nam-nam fruit meat that has been ground into the frying pan, vi) fry the nam-nam fruit meat until it becomes darkened and smoke co mes out of the frying pan, vii) lift the material from the frying pan, viii) separate the material and c ooked oil with a sieve and a filter paper, ix) insert three drops of the cooked oil into 5 ml of n-hexa ne solution and stir it evenly.

The procedure of synthesizing Cdots/S is given as follows: i) weigh 2.5 grams of sulphur powder, ii) add the weighted sulphur powder into a 100 ml of the previously cooked oil from the nam-nam fruit, iii) heat the cooked oil for 15 minutes with a temperature of 100 ^{o}C until the cooked oil becomes red in color, iv) stir the cooked oil until evenly distributed, and v) drop a sample of three drops of the cooked oil with a pipette into 5 ml of n-hexane.

UV-Vis Spectrophotometer test is used to find out the absorption of the samples. The UV-Vis equipment used is the UV-2400PC series. X-ray diffraction (XRD) testing is conducted upon thin layer fabrication of the samples on glass substrates. The XRD device used is Rigaku Miniflex600 with operating conditions of 40 kW, 15 mA, and using Cu light. Photoluminescence (PL) testing is carried out upon samples in the form of solutions. PL testing is used to determine the wavelength of emissions produced by the samples. The PL equipment used is Spectrophometers MayP112615 spectrum 2068 with a laser at a wavelength of 420 nm. Finally, TRPL characterization is done to find out the emission time of the Cdots and Cdots/S samples using the same PL equipment.

3. Results and discussion

The results of the Cdots and Cdots/S samples synthesized via the frying method produce different color solutions. The Cdots solution before being dissolved in n-hexane has a greenish color [Fig. 2(a)]. The Cdots/S solution has a dark-reddish color as shown in Fig. 2(b). The Cdots and Cdots/S solutions are further dissolved in n-hexane solution. N-hexane is an inert and non-polar solvent, which can dissolve oil. The results of the Cdots and Cdots/S solutions dissolved into n-hexane are shown in Figs. 2(c) and 2(d). It may be observed that the Cdots solution in n-hexane is clear (colorless), while the Cdots/S in n-hexane is darker compared to the Cdots solution in n-hexane.

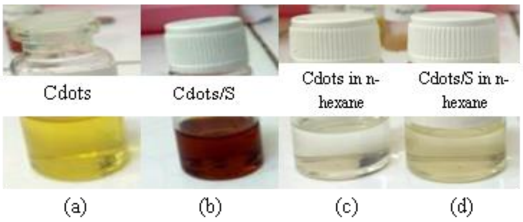
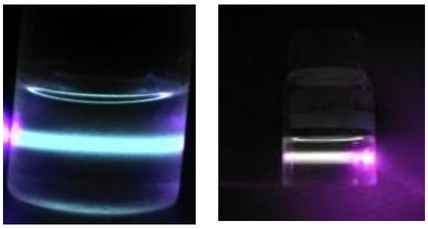


Fig. 2.Various samples obtained: Cdots (a); Cdots/S (b); (c) Cdots in n-hexane (c), and Cdots/S in n-hexane (d).

The samples, which have been synthesized, are then characterized using several tests. A simple test is done by exposing a laser (405 nm and 5 mW max output power) to the samples, which is shown in Fig. 3. Fig. 3 shows that both Cdots and Cdots/S have the same green luminescence color but with different intensities. The highest luminous intensity is qualitatively the Cdots solution and then the Cdots/S. The samples are then quantitatively characterized using UV-Vis, PL, TRPL, and XRD.



(a) (b)

Fig. 3. Samples of Cdots (a) and Cdots/S (b) exposed by a laser.

UV-Vis spectroscopy is used to identify absorbance patterns at specific wavelengths. The UV-Vis characterization graph is a relationship between wavelength (nm) and absorbance. Measurements are made at 200 nm to 800 nm wavelength intervals with n-hexane as the blank (standard) solution and Cdots and Cdots/S in n-hexane as the sample solutions. The results of the characterization of the two samples are shown in Fig. 4. This figure shows the UV-Vis spectrum profiles comparison between Cdots and Cdots/S.

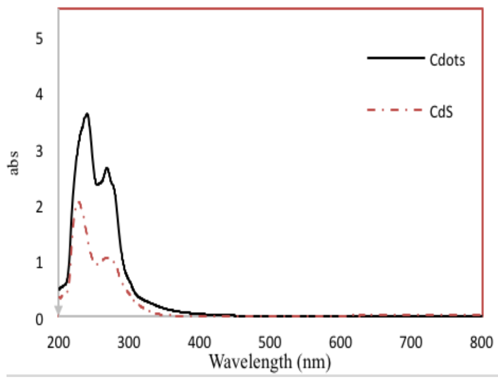


Fig. 4. Results Characterization of Cdot and Carbon dots/Sulfur with UV-Vis.

Based on Fig. 4, there are two main peaks at wavelengths of 268 nm and 242 nm for the

UV-Vis of Cdots solution (solid-black line). This shows that there are two electronic transitions, which are the excitation of electrons at the lower states (HOMO) towards higher states (LUMO). Furthermore, the molecular transition is the π - π^* transition which shows the conjugation in the Cdots structure [12]. The Cdots that have been synthesized is said to be successful because there is a peak at 268 nm. This is based on a previous study that Cdots synthesized by physical and chemical methods shows one or two absorbance peaks at 260 nm to 360 nm in the UV range for UV-Vis spectroscopy [13]. Furthermore, the addition of sulphur into the Cdots, i.e. Cdots/S shown in Fig. 4 with dashed-red line for its UV-Vis results, resulted in the decrease of the absorbance values compared to Cdots solution. In addition, there are two absorbance peaks for the Cdots/S solution of 268 nm and 228 nm. The peaks show the same results as for the Cdots solution, namely that there are two molecular transitions, which are electron excitations from HOMO to LUMO. In addition, the difference at the first peak for the Cdots and Cdots/S does not occur significantly, while a shift occurs at the second absorption peak after the addition of sulphur, which is from 242 nm (Cdots) to 228 nm (Cdots/S).

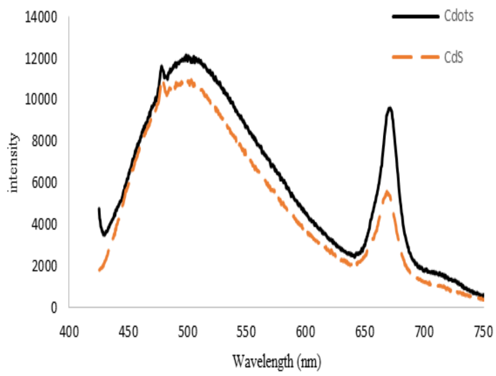


Fig. 5. Graph of PL characterization.

PL characterization is related to the molecular transitions from an excited state to the ground state. The PL spectrum shows a relationship between the intensity and the emission wavelength. For the Cdots and Cdots/S solution samples, the PL characterization is performed with an excitation wavelength of 420 nm. The results of the PL characterization of the samples are shown in Fig. 5. The figure shows that at the same solution concentration of the Cdots (solid-black line) and Cdots/S (dashed-red line) samples, the intensity of the PL spectrums is different. Furthermore, Fig. 5 shows two dominant peaks occurring from the PL characterization for both samples, that is the first peak in the range 490 nm to 520 nm and the second peak at 660 nm to 690 nm. The first peak for the Cdots sample is at a wavelength of 497.87 nm, while the addition of sulphur shifts the peak to longer wavelength of 498.79 nm. This means that the addition of sulphur produces a small amount of emission change. Moreover, the Cdots solution synthesized produces a luminous color of green because the green color has luminescence within the range of 495 nm to 570 nm. Furthermore, this is in accordance with the qualitative results of the UV-irradiated samples in Fig. 3. Fig. 5 also shows that there is no significant wavelength change in the addition of sulphur to the Cdots solution. However, the addition of sulphur affects the intensity of the color produced in Cdots/S, which is supposedly corresponds to the number of Cdots/S particles produced. Addition of sulphur can decrease the transmission of the Cdots solution. Furthermore, the second dominant peak, i.e.: at the wavelength of 650 nm to 700 nm is produced by another material in the solution. According to a study by Li *et al.* (2017), which successfully synthesizes Cdots derived from spinach leaves, the PL peak resulted from the study is 670 nm indicating a porphine structure [14]. The porphine structure is a molecule contained in chlorophyll; hence the Cdots derived from the nam-nam fruit still contain chlorophyll. The chlorophyll still exists when the frying is conducted, which is then dissolved in the oil.

The Cdots and Cdots/S solutions are then characterized using TRPL. The excitation source used is a UV laser with a wavelength of 420 nm. Characterization of the samples using TRPL aims to determine the overall time of electrons or the time required for the electrons to return to the valence band. Furthermore the data is fitted using exponential decay-1 (via Origin software) to determine the total time of electrons to return to the valence band. This may be observed in Fig. 6. The fitted results based on Fig. 6 show that the de-excitation times of Cdots and Cdots/S samples are equal to 2.46 ± 0.02 ns and 1.71 ± 0.02 ns, respectively. These data show that the addition of sulphur to the Cdots affect the de-excitation time of the electrons that is it shorten the electron's decay time.

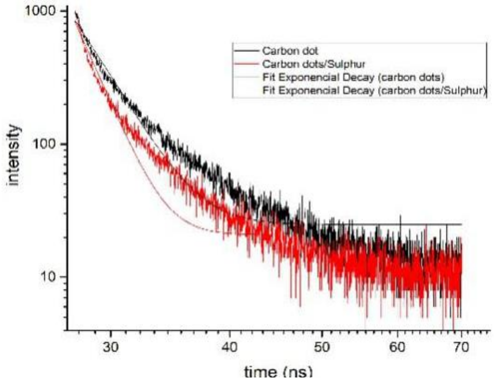


Fig. 6. Characterization results of Cdots (solid-black profile) and Cdots/S (solid-red profile) with TRPL.

The characterization via XRD is used to know the crystallinity of materials. The source used is Cu kα with a wavelength (λ) of 0.15418 Å and the range used is 2° to 80°. The data of the test results produce a diffractogram, which shows a relationship between the scattering angle (2θ) and intensity (I). In this case we have to identify the peaks in the spectrum. The samples used in this XRD test are the solidified Cdots and Cdots/S solutions. This may be observed in Fig. 7. Fig. 7 shows that the samples that have been synthesized are amorphous. This is because the diffractograms does not indicate specific or distinctive peaks at a certain angle, so the distance between atoms has no pattern and tends to be random. However, there are 'bumps' at 2θ around 10° to 35° for both samples.

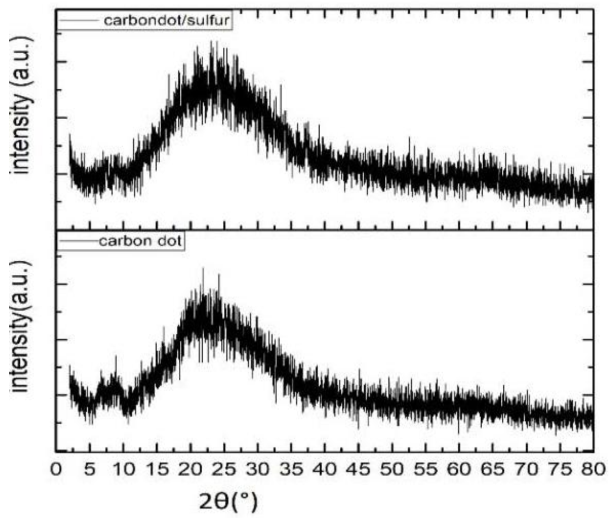


Fig. 7. Characterization results of Cdots (bottom profile) and Cdots/S (top profile) using XRD.

4. Conclusions

Synthesis and characterization of Cdots and Cdots/S from nam-nam fruit via oil based frying method has been conducted. The characterization of Cdots and Cdots/S samples is done by UV-Vis, PL, TRPL, and XRD. The UV-Vis testing on Cdots shows two peaks at 242 nm and 268 nm, whereas for Cdots/S yields absorbance peaks at 228 nm and 268 nm. The PL results of the two samples produce two different peaks. The first peak shows a green color transmission of 497.87 and 498.79 nm for Cdots and Cdots/S solutions, respectively. The second peak of the PL indicates porphyrine group having wavelengths of 668.02 nm and 670.27 nm for Cdots and Cdots/S, respectively. The TRPL test results show that the addition of sulphur shortens the duration of the electron decay. Finally, the XRD test results show that the samples are amorphous as no peaks occur in their diffractograms.

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