

# SYNTHESIS OF CARBON NANOPARTICLES (C-DOTS) FROM NATURAL DYES AND ITS CHARACTERISTICS

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Carbon nanoparticles (C-dots) are one of the results of the development of nanotechnology that began in 2004. C-dots have the property of being able to fluoresce. C-dots have the potential to replace other nanoparticles, such as quantum dots. C-dots had the same applications as quantum dots but not toxic so that they can be applied more widely in various sectors. C-dots can be synthesized from a carbon-based precursor. The quality of C-dots can be enhanced with carbon-based organic compounds that have conjugated systems and contain heteroatoms, one of which is a natural dye compound. The synthesized method can influence the properties of C-dots. This article reviewed the literature on the synthesis of C-dot from natural plant dye precursors. The results showed that the C-dots synthesized from tannin had better quality than other dye compounds. The solvothermal method improves the quality of C-dots as solvent provides extra functional groups.

Keywords: C-dots, fluorescent, natural dye, solvothermal, tannin

## INTRODUCTION

C-dots were found in 2004, and they have very interesting advantages (Li et al. 2012). The advantage of C-dots is that they have the physical properties of being able to fluoresce or emit light. C-dots have the potential to replace other nanoparticles, especially quantum dots which have developed earlier than C-dots. C-dots have characteristics and functions that are almost the same as quantum dots, but C-dots are not toxic (Baker and Baker 2010). C-dots have other advantages, such as high solubility in water, low toxicity, inertness, high biocompatibility, and good fluorescence stability (Xu et al. 2015). C-dots in its application are used as biolabeling, biomedical, sensors, photocatalysts, and photoelectronic equipment (Zhang et al. 2017).

C-dots can be synthesized through top-down and bottom-up methods. The top-down method is a method of forming nano-sized C-dots from a larger carbon structure. The bottom-up method is the formation of nano-sized C-dots from certain precursor compounds. Top-down methods include arc discharge, laser ablation, and electrochemical oxidation. The bottom-up method consists of microwave, hydrothermal, chemical ablation, and electrochemical carbonization. In general, the surface of C-dots is oxidized by nitric acid (HNO<sub>3</sub>) or sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and then purified by centrifugation, dialysis, electrophoresis (Baker and Baker 2010).

The synthesis of C-dots started from the purification of single-walled carbon nanotubes in 2004 using the gel electrophoresis method to obtain carbon nanotubes measuring 10 nm and fluorescing (Xu et al. 2004). After that, the synthesis of C-dots can use activated carbon (Dong et al. 2010), carbon fiber (Bao et al. 2011), and graphite (Liu et al. 2016). The main precursor for the synthesis of C-dots is a material having a carbon source. The carbon source can come from chemical compounds such as organic acids. Examples of organic acids that have been used in the synthesis of C-dots are citric acid (Zhu et al. 2015) and amino acids (Huang et al. 2014). One material that has the potential to be a precursor for the synthesis of C-dots is plant body parts. The majority of plant body parts used as precursors for C-dots synthesis are onion skin (Triwardiati and Ermawati 2018), lychee seeds (Xue et al. 2015), durian (Anindita 2018), sago pulp (Setiadi 2017), and mango leaves (Qurrata et al. 2018). Plant body parts have many

advantages as a carbon source, because they contain a lot of carbon from carbohydrates, fats, proteins, and some amino acids.

Fluorescence is one of the superior properties of C-dots. The fluorescence properties of C-dots are influenced by several factors, including the constituent functional groups and the surface state of the C-dots. The functional group components that make up the C-dots can be obtained from the synthesis process with carbon precursors of organic compounds, and can be increased by the presence of functional groups that have a conjugate system (Zhang et al. 2014). One material that has a compound with a conjugation system is a natural dye. Examples of these compounds are anthocyanins, chlorophyll, beta crytoxanthin, myricetin, quercetin, and various other compounds. The use of natural dyes in the product industry has been replaced by dyes from synthetic chemicals, so that the presence of natural dyes is abundant and some of them become biomass waste. Therefore, natural dyes are very cheap and environmentally friendly precursors of synthetic C-dots.

The state of the C-dots surface can be influenced by the functional groups and atoms that make up the C-dots surface. The presence of functional groups and atoms on the surface of C-dots can be modified through the addition of passivation agents and heteroatom doping (Li and Dong 2018). A passivation agent is a material that serves to increase the content of certain functional groups on the surface of C-dots so as to increase the luminescence and solubility of C-dots. This research was conducted to determine the potential of C-dots precursors from natural dyes and to improve the surface quality of C-dots in terms of several characteristics including, quantum yield (QY), emission, and functional groups on the surface.

## **MATERIALS AND METHOD**

The literature reviewed is based on data from various previous research results related to the synthesis of C-dots with natural dye compounds, the quality of C-dots, and the effect of synthesis methods and heteroatom doping on C-dots. Library data are obtained from national and international scientific journals, dissertations, theses, and theses from previous research whose truth can be accounted for. The tools used are laptops, Microsoft Office Applications, Mozilla Firefox Browser, Mendeley, and Photoshop.

This research uses a systematic literature review method. Secondary data retrieval through literature study and literature review from several scientific journals, dissertations, theses, theses, and research works that have been done previously and the truth of the information can be accounted for. The majority of literature publications used range from 2011–2021, with publications in 2004–2010 as historical supporting evidence.

The provisions of the material studied in this study are as follows: the studies carried out include the potential for synthesizing C-dots using natural dyes, the effect of the C-dots synthesis method, and the effect of passivation and atomic doping processes on the synthesized C-dots; The characteristics of C-dots used as components include quantum yield, emission, and functional groups on the surface.

Collection of library resources by downloading libraries from the internet through the Google Scholar page, sciencedirect.com, researchgate.com, IPB repository and other universities, as well as various other trusted sites. The library sources that have been obtained are then analyzed and selected in accordance with the provisions of the library sources. Sources of literature in accordance with these provisions, are reviewed and reviewed according to the studies that have been determined. The results of the study are described in a thesis template with the author's point of view.

## **RESULTS AND DISCUSSION**

Carbon nanodots (C-dots) are one of a new class of nanomaterials that can fluoresce. C-dots have a composition that can be used for metals and have good biocompatibility, so they

are non-toxic and can be used in wide applications (Tuerhong et al. 2017). C-dots were discovered accidentally during the purification of single walled carbon nanotubes from soot by the gel electrophoresis method (Xu et al. 2004). C-dots have a quaspherical shape with a size of 10 nm so that it includes zero-dimensional nanoparticles (Baker and Baker 2010). C-dots have sp<sup>2</sup> and sp<sup>3</sup> hybridization, so that in C-dots there is a conjugated system (Li et al. 2012). C-dots are divided into two parts, namely the core which is inorganic carbon with C=C, C-C bonds, and the surface that is attached to the core. The surface consists of various functional groups (Liu et al. 2007), shown in Figure 1. These functional groups produce certain physical, chemical, and optical properties that can support the application of C-dots. The functional groups, namely alcohol, carboxylic acid, and amino are affected by the solvent used or additional precursors (Zhao et al. 2008).

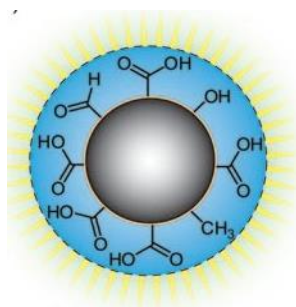


Figure 1 The structure of C-dots (Baker and Baker 2010)

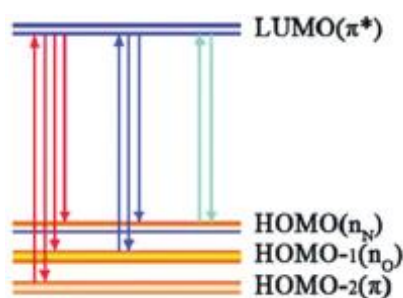


Figure 2 Jablonski Diagram (Liu et al. 2019)

The quality of the synthesized C-dots can be evaluated through several characteristics, namely emission, functional group, and quantum yield. These three characteristics are closely related and center on fluorescence emission. Fluorescence is the process of emitting light radiation by a material after being excited by a high-energy light beam (Zain et al. 2007). Each atom will experience excitation to the Lowest Unoccupied Molecular Orbital (LUMO) when exposed to high-energy rays. Excited atoms will relax to their original state or Highest Occupied Molecular Orbital (HOMO) by releasing light energy (emissions) as shown by the Jablonski Diagram in Figure 2 (Liu et al. 2019). C-dots fluorescence emission provides a variety of color visualizations. This is influenced by the amount of energy emitted so that it affects the wavelength of light which has implications for color visualization. The amount of energy emitted depends on the amount of energy absorbed in the excitation process which is mainly influenced by the state of the C-dots (Triwardiati & Ermawati 2018). The color visualization produced by C-dots will affect the application of C-dots. C-dots with red emission have a wider application especially in bioimaging (Ding et al. 2017).

Based on Liu et al. (2019), there are three fluorescence mechanisms on C-dots. The first is the surface state of the C-dots which includes, the level of oxidation and the surface functional groups. The degree of oxidation and surface states with superior functional groups such as amides, aminos, and carboxylic acids can lead to increased surface defects that can trap excitons and capture exciton recombination radiation, thereby causing a red shift because the band gap decreases as surface oxidation increases as evidenced in Figure 3 Second, the quantum

confinement effect described by the conjugated domain. The conjugated domain is affected by the size of the nanoparticles. The larger the size of the nanoparticles, the distribution of electrons will also be greater so that the conjugated domain is getting bigger. This causes a decrease in the band gap so that the resulting wavelength will be larger. Third, molecular fluorescence. Molecules that can fluoresce or are called fluorophore molecules will produce certain emissions, but the emission of fluorophore molecules can be interfered with by impurity molecules obtained from the by-products of the C-dots synthesis process so that they can block the emission of fluorophore molecules. Therefore, perfect purification is required to produce high-intensity fluorescence by this mechanism.

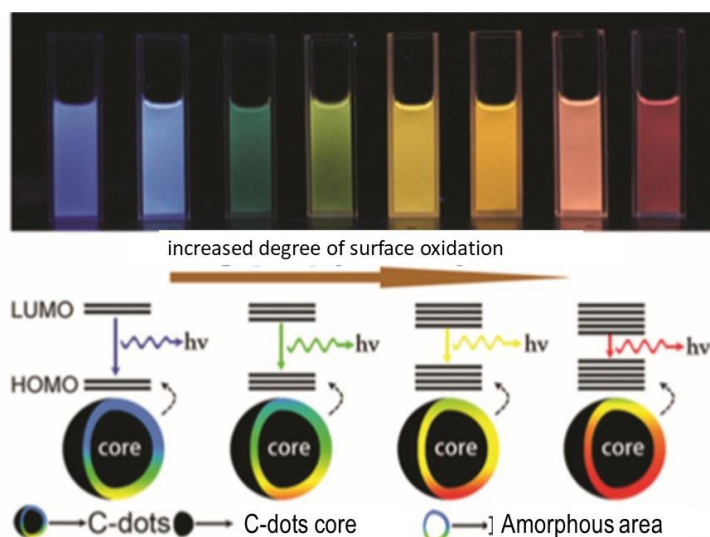


Figure 3 Relationship between band gap and surface oxidation (Liu et al. 2019)

Bao et al. (2015), conducted an experiment which stated that the fluorescence of C-dots based on the band gap can be influenced by the surface properties and size of the C-dots. The fluorescence mechanism that is mostly used as a reference is the first and second mechanisms. As a result, most of the fluorescence properties of C-dots can be controlled by adjusting the size of the carbon core and surface functional groups. Therefore, functional groups have a major role in the fluorescence properties of C-dots. C-dots generally have functional groups such as carboxylic acids, aldehydes, alcohols, and carbonyls (Kwon et al. 2015). C-dots containing amide, amine, and carboxyl functional groups produce superior properties compared to other C-dots (Ji et al. 2019). In addition, the  $\pi$ -electron system (Bao et al. 2015) and the electron conjugation system (Zhang et al. 2014) can enhance the fluorescence properties of C-dots. The increase in oxygen on the surface of the C-dots can increase the degree of oxidation on the C-dots which is proportional to their fluorescence properties. The overall state of the C-dots surface, especially the functional groups present on the surface, has a significant effect on the fluorescence properties of C-dots.

The most important parameter to evaluate the fluorescence of C-dots is the quantum yield (QY). Quantum yield is the ratio of the number of photons emitted to the number of photons absorbed per unit time. In simple terms, QY is the ratio of the luminescence intensity of the sample to the standard compound. The standard compound requirements that can be used are compounds that have absorption and emission spectra that are comparable to C-dots. The excitation spectrum of C-dots and standard compounds such as plateaus or at least the wavelengths on the absorption spectrum gradient is flat (Grabolle et al. 2009). Commonly used standards are sodium fluorescein, rhodamine B, and quinine sulfate. The following is the equation for determining QY in the synthesis of C-dots conducted by Hoan et al. 2019.

$$QY_x = QY_{st} \frac{m_x}{m_{st}} \times \frac{n_x^2}{n_{st}^2}$$

st and x represent the standard and sample, m is the gradient of the integrated luminescence intensity equation to absorbance, and n is the refractive index.

**Literature Review of Synthesis of Carbon Nanodots from Precursors of Natural Plant Colorants.** Plants contain various carbon compounds such as flavonoids, phenolics, and amino acids. C-dots synthesized from plant precursors have better fluorescence properties than chemical precursors. This is because most of the compounds in plants have conjugated functional groups such as flavonoid compounds. In addition, some compounds also contain nitrogen and sulfur atoms such as amino acids. Nitrogen and sulfur atoms can facilitate the heteroatom doping process without the addition of certain compounds/solvents, so as to improve the surface condition of the C-dots better. This results in an increase in the fluorescence properties produced (Zhang et al. 2017). One of the compounds in plants that contain conjugated functional groups and certain heteroatoms that can be used for heteroatom doping is a group of natural dyes.

Natural dyes are dyes derived from natural ingredients which are generally produced from plant or animal extracts (Ikhsanti and Hermawan 2020). Natural dyes from plants can be obtained from all parts of the plant body, such as leaves, stems, seeds, fruit skins, and flowers. Natural dyes have certain active compounds that contain heteroatoms and functional groups with a conjugate system. Heteroatoms in these dye compounds can be used for heteroatom doping. This causes C-dots synthesized from natural plant dyes to have better fluorescence properties. Synthetic dye compounds also contain heteroatoms and functional groups with a conjugated system, but natural dye compounds are richer in other compounds that can increase the functional group content of the C-dots surface. Examples of natural dyes used as precursors for the synthesis of C-dots are shown in Table 1.

Research on the synthesis of C-dots using natural dye precursors has only begun in the last six years. Most of the methods used for the synthesis of C-dots from natural dyes are bottom-up methods. Natural dyes include biomass that can be polymerized and carbonized at high temperatures to form C-dots (Liu et al. 2019). The most widely used bottom-up methods are hydrothermal (60%) and solvothermal (25%). This is because both methods can synthesize C-dots from biomass with a temperature that is not too high through pressure regulation (Gupta and Tripathi 2012). The hydrothermal and solvothermal methods have the same basic principle. The two methods have differences in the solvent. The hydrothermal method is a bottom-up method with water as a solvent, while the solvothermal method uses an organic solvent (Lalena et al. 2008). The quality of C-dots synthesized by hydrothermal and solvothermal methods is influenced by the duration of the synthesis time, the temperature used, and the number of precursors. These factors can have direct implications for the photoluminescence properties of C-dots (Zulfajri et al. 2019).

The hydrothermal and solvothermal methods have not been found with certainty and details regarding the mechanism. The processes that occur in the formation of C-dots from biomass through these methods are hydrolysis, dehydration, and decomposition of biomolecules that make up precursors to produce compounds. certain compounds that are soluble in the solvent used. After that, the polymerization and condensation processes will occur, producing more soluble polymer products, then the aromatization and carbonization processes will go through several reactions and then produce inorganic carbon that has various aromatic structures or C-dots (De and Karak 2013). In addition, passivation processes can occur through the addition of passivation or functionalization agents and precursors containing heteroatoms (Li and Dong 2018). The advantages of the hydrothermal method are that it is environmentally friendly, easy to work with, simple, stable, inexpensive, low energy consumption, and easy to control through size, composition, purity, and energy (Pal et al. 2018). Solvothermal method is more expensive than hydrothermal, because it uses organic solvents. The solvothermal method has the advantage of being able to produce products without interfering ions, because it has a low permittivity. In addition, the solvothermal process produces products with high chemical homogeneity and a unique metastable structure at low temperatures (Gupta and Tripathi 2012).

Table 1 Summary of literature review on the synthesis of C-dots from natural plant dyes with various methods

Method	Precursor	Solvent	Active Compounds	QY (%)	Emission (nm)	References
Solvothermal	Lemon juice	Etanol	Tannin	28	631	Ding <i>et al.</i> (2017)
	Malus floribunda fruit	Ammonia	Antocyanin	18	418	Atchudan <i>et al.</i> (2020)
	Indian Goose-berry	Ammonia	Tannin	13,5	411	Atchudan <i>et al.</i> (2018)
	Prunus- avium	Ammonia	Antocyanin	13	411	Nesakumar <i>et al.</i> (2016)
Hydrothermal	Lemon juice	Aquadest	Tannin	14,9 <sup>a</sup>	550 <sup>a</sup>	Hoan <i>et al.</i> (2019)
				16,9 <sup>b</sup>	540 <sup>b</sup>	
				21,4 <sup>c</sup>	518 <sup>c</sup>	
				24,9 <sup>d</sup>	508 <sup>d</sup>	
	Rose-heart radish	Aquadest	Antocyanin	13,6	420	Liu <i>et al.</i> (2017)
	Ocimum tenuiflorum Tulsi) leaf extract	Aquadest	Chlorophyll	11,5	405	Shukla <i>et al.</i> (2019)
	Cranberry beans	Aquadest	Proanthocyanidin	10.8	450	Zulfajri <i>et al.</i> (2019)
	Sweet potato	deionized water	Antocyanin	8,6	442	Shen <i>et al.</i> (2017)
Pomegranate	Aquadest	Antocyanin	7.6	453	Kasibabu <i>et al.</i> (2015)	
Strawberry juice	Aquadest	Antosianin	6.3	427	Huang <i>et al.</i> (2013)	
Tulsi leaves	Milli-Q water	Chlorophyll	3,1	435	Bhatt <i>et al.</i> (2018)	
Microwave	Rose flower	Aquadest	Antocyanin	13,45	435	Feng <i>et al.</i> (2015)
Pyrolysis	Borassus flabellifer	Milli-Q water	Antocyanin	13.97	320	Murugan and Sundramoorthy (2018)
Ultrasonic	A. indica, O. tenuiflorum, and T. procumbens leaves	H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub>	Chlorophyll	-	518	Meena <i>et al.</i> (2019)

<sup>a</sup>C-dots temperature treatment 150 °C <sup>b</sup>C-dots temperature treatment 200 °C <sup>c</sup>C-dots temperature treatment 240 °C <sup>d</sup>C-dots temperature treatment 280 °C

Based on the QY parameters from Table 1, the best C-dots using the solvothermal method were C-dots from the lemon and Malus floribunda fruit precursors. C-dots from lemons were synthesized by Ding *et al.* (2017) with ethanol solvent at 190 °C for 10 hours and C-dots from Malus floribunda fruit were carried out by Atchudan *et al.* (2020) at 200 °C for 12 hours. Lemon contains an active compound of tannins, while the fruit of Malus floribunda contains anthocyanin as an active compound. The QY C-dots of lemons are 28%, while those of Malus floribunda are 18%. The QY difference between the two C-dots is quite significant. The

functional groups that make up the C-dots surface can be identified through the bonds obtained from the FTIR characterization. The results of the FTIR spectrum can be seen in Figure 4. The FTIR spectrum of C-dots from lemon and *Malus floribunda* fruit states that the bonds in the two C-dots are almost the same, there are 7 signal peaks with the same three bonds, namely C-H, C=C, and C-N. The signal difference is indicated by the different binding of the two C-dots. The C-dots of the lemon indicate the presence of N-H, CO-OH, and C-O bonds. C-dots of *Malus floribunda* have C=O, C-OH, and C-O-C bonds.

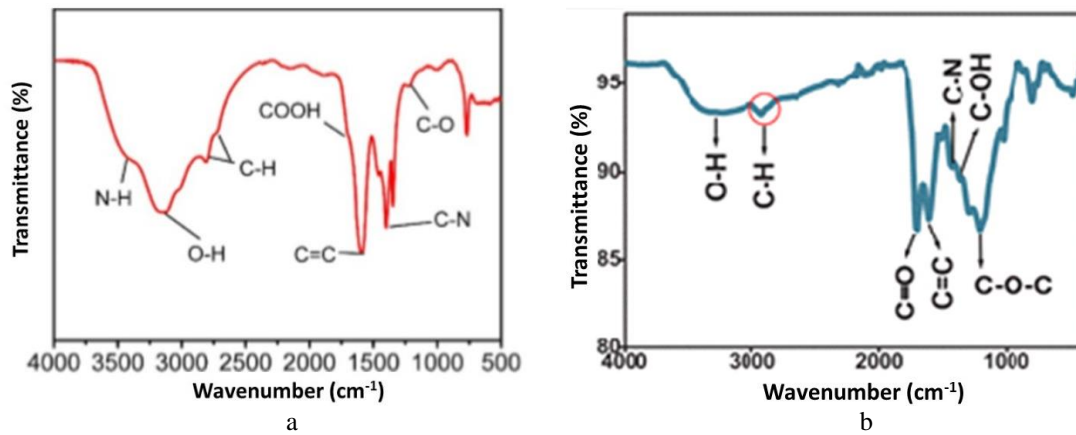


Figure 4 FTIR spectrum of C-dots with precursors a) lemon (Ding et al. 2017) and b) *Malus floribunda* (Atchudan et al. 2020)

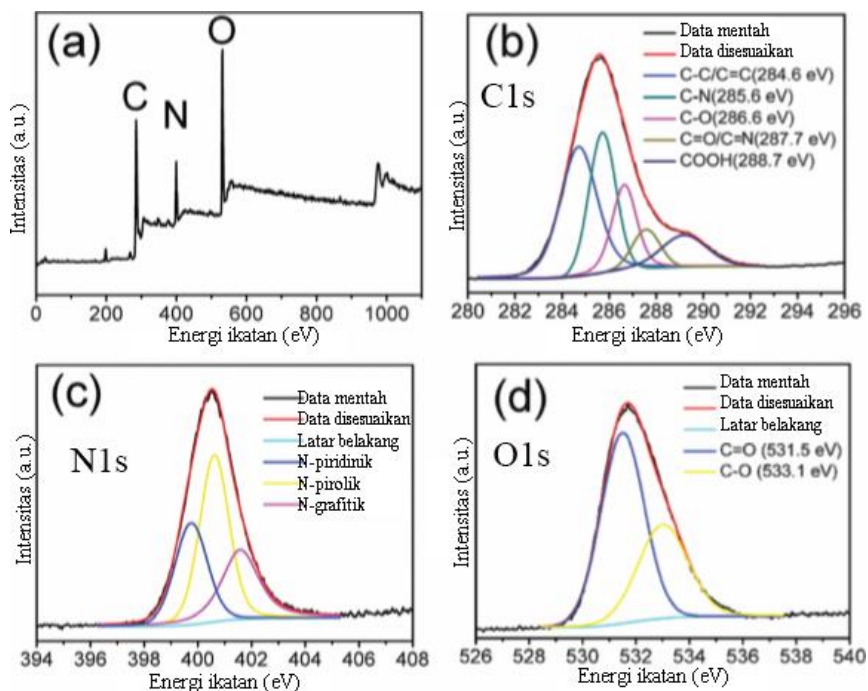


Figure 5 XPS Spectrum a) C-dots of lemon, b) high resolution at C1s, c) high resolution at N1s, d) high resolution at O1s (Ding et al. 2017)

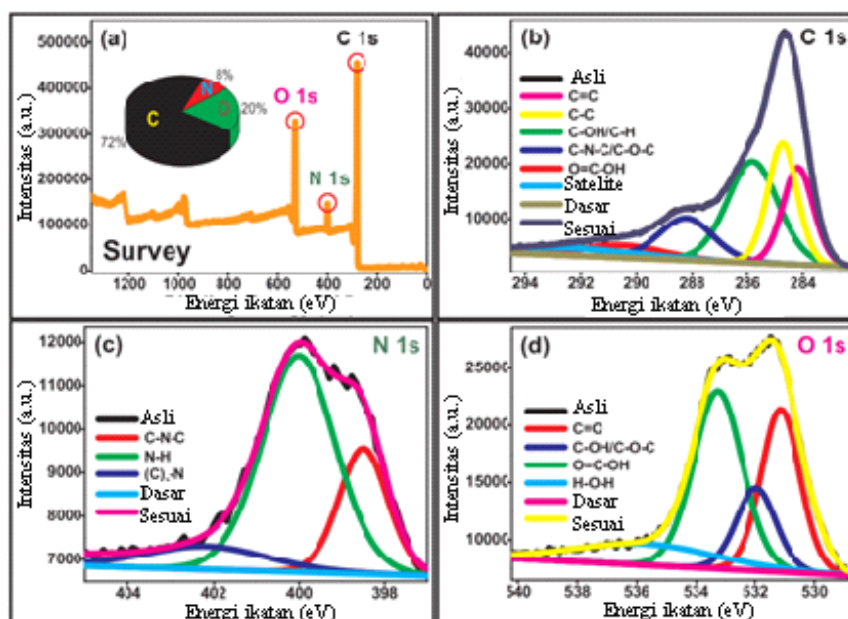


Figure 6 XPS Spectrum a) C-dots of *Malus floribunda*, b) high resolution at C1s, c) high resolution on N1s, d) high resolution on O1s (Atchudan et al. 2020)

The presence of amine and amide groups on the C-dots of lemon was caused by the thiamine content in lemon which has a pyrimidine main ring, while the amino groups that appeared in the FTIR spectrum of C-dots of *Malus floribunda* came from the ammonia solvent used in the synthesis. The CO-OH bond on the C-dots of lemon is thought to come from ethanol which functions as a solvent. The FTIR spectrum is supported by the XPS spectrum in Figure 5 and Figure 6, which states that the nitrogen composition of C-dots from lemon reaches 15% while C-dots from *Malus floribunda* contains 8% nitrogen. In addition, the oxygen composition of the C-dots of lemon is higher than that of carbon because the tannin compounds contain a higher number of carbonyl functional groups. This shows that the C-dots have a very high degree of oxidation. C-dots of *Malus floribunda* have a higher carbon composition than oxygen. This is because the active compound anthocyanin has a large number of carbons with the structure listed in Appendix 3, so that the carbonization is more complete. The proportions of the atoms of the two C-dots experienced a significant difference, but the bonds formed were almost the same only experienced a difference in intensity

The implication of the difference in bond content is the difference in emission wavelengths emitted by the C-dots. The active compounds in lemon are tannins which have a wavelength of 440–600 nm (Sari et al. 2015). The C-dots of lemon are excited at a wavelength of 300–500 nm, then emitted in the wavelength range 600–675 nm as shown in Figure 7a, thus emitting a red emission. The maximum emission intensity is at wavelength 640 nm with an excitation wavelength of 540 nm. The active compound contained in the fruit of *Malus floribunda* is anthocyanin, with a wavelength of 515–545 nm. C-dots of *Malus floribunda* are excited at a wavelength of 300–500 nm. Fluorescence is emitted in the 395–545 nm wavelength range shown in Figure 7b. The maximum emission wavelength is at 418 nm with excitation at 340 nm.

C-dots of lemon and *Malus floribunda* result in an increase in the emission wavelength when the excitation wavelength increases. This indicates a red shift (bathochromic) between the emission spectra of the two C-dots. The bathochromic shift in C-dots of lemon was greater than that of C-dots of *Malus floribunda*, due to the presence of nitrogen heteroatoms in pyridinic, pyrrolic, and graphitic forms as shown in Figure 6c. In addition, the degree of surface oxidation on C-dots lemon is higher than C-dots *Malus floribunda*. This causes a decrease in the band gap and an increase in the emission wavelength to the red region. N-pyridinic is the N between two C atoms that donates one p electron to the system, while N-graphitic is the N atom that replaces



the C atom in the hexagonal ring. N-pyrolic is N that donates two electrons to the system and bonds to a five-membered ring (Zhang et al. 2011).

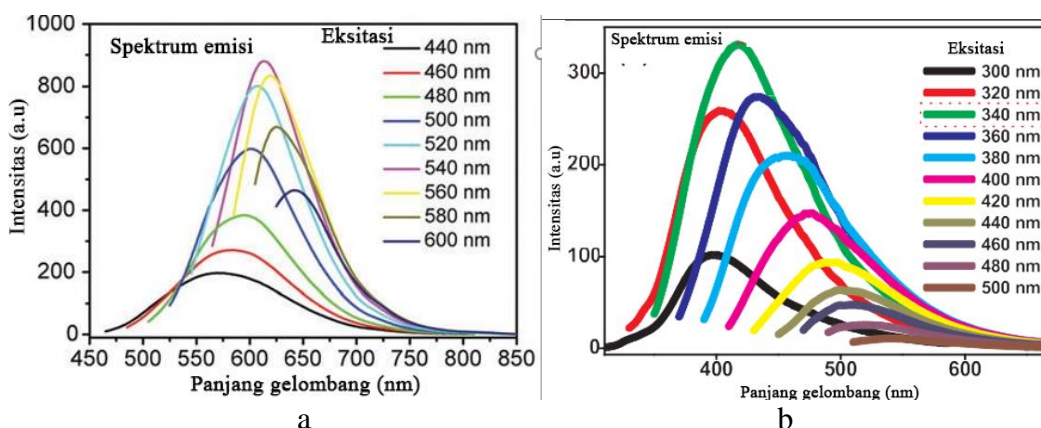


Figure 7 Photoluminescence emission spectrum and the excitation wavelengths that affect it a) C-dots from lemon (Ding et al. 2017), b) C-dots from Malus floribunda (Atchudan et al. 2020)

C-dots Malus floribunda also undergo bathochromic shifts between its spectra but in very small amounts, caused by nitrogen doping that formed N-pyridinic, N-graphitic, and N-amino. In addition, the fluorescence intensity produced by C-dots lemon has a much greater intensity compared to C-dots lemon. This is caused by the nitrogen content doped in C-dots lemon is greater than C-dots Malus floribunda. The bonds and heteroatoms contained in the C-dots are not very superior so they have little effect on the fluorescence process. Based on the comparison of the quality of the two C-dots, it was found that nitrogen doping was better using precursors containing amine or amide functional groups. It is better to increase the degree of oxidation on the C-dots surface using a precursor that contains a lot of oxygen and can be supported by the use of an oxygen-containing solvent. The active compounds of natural dyes that are better used as precursors of C-dots using the solvothermal method are tannins.

Based on Table 1, Hoan et al. (2019) conducted an experiment on the synthesis of C-dots from lemon and Liu et al. (2017) carried out the synthesis of C-dots from red radish to produce C-dots with the best quality from the hydrothermal method. Hoan et al. (2019) synthesized C-dots using four temperature variations, namely 150, 200, 240, and 280 °C for 12 hours. Liu et al. (2017) carried out the synthesis of C-dots from red radish which contains the active compound anthocyanin natural dye. Synthesis of C-dots was heated at 180 °C for 3 hours. C-dots of lemon in the discussion focused on C-dots treated at 150 °C for 12 hours. This was done in order to make adjustments to the C-dots synthesis carried out by Liu et al. (2017). The QY C-dots of lemons are 14.86%, while the QY C-dots of radishes are 13.6%.

There was a difference in the FTIR spectrum on the C-dots of lemon and red radish. Figure 8 shows that C-dots from lemon contain CO-OH, C=O, C-H, and C-O-C bonds, while Figure 9 shows C-dots from red radish have NH, CH, CO-O, C=C, and C-O bonds. Both have in common in the C-H bond only. Based on the figure, it can be seen that the type of bond formed is more in the C-dot than the red radish. In addition, the C-dots of red radish contained doped nitrogen heteroatoms as shown in the FTIR spectrum. However, the QY C-dots of lemon were greater than the C-dots of radish. This was due to the longer hydrothermal time of C-dots synthesis from lemon which resulted in more and more carbonization of the constituents of the precursor. In addition, lemons contain high concentrations of citric acid which serves as a source of carbon and other functional groups apart from the active compound tannins. The intensity of the bonds formed on the C-dots of the lemon is also higher, thus increasing the intensity of the resulting emission.

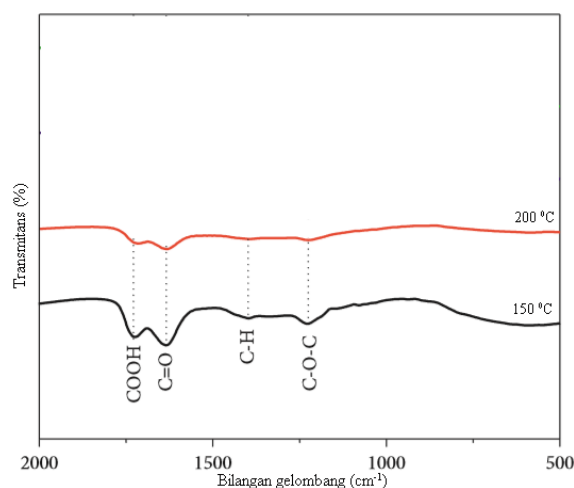


Figure 8 FTIR C-dots spectrum from lemon hydrothermal method with temperatures of 150 and 200 °C and a time of 12 hours (Hoan et al. 2019)

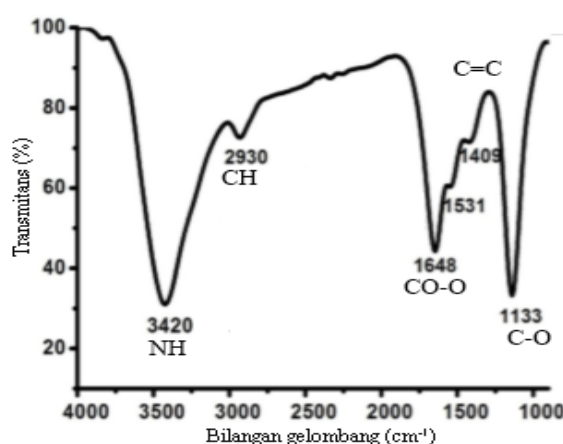


Figure 9 FTIR C-dots Spectrum of red radish (Liu et al. 2017)

The emission of C-dots from lemon has a wavelength in the range of 500–600 nm with an excitation wavelength of 360–480 nm. The maximum emission intensity is at a wavelength of 550 nm with an excitation at 480 nm as shown in Figure 10. C-dots of red radish have an emission wavelength of 350–550 nm with an excitation wavelength of 280–500 nm. The maximum emission intensity is at a wavelength of 420 nm with an excitation wavelength of 330 nm which is shown in Figure 11. Based on these data, it is stated that there is a bathochromic shift in the second emission wavelength of C-dots along with the increase in the excitation wavelength. However, the bathochromic shift in the lemon C-dots was very small compared to the red radish C-dots. This is caused by the presence of nitrogen doping with N-H bonds on the C-dots of red radish, so that it can increase the wavelength shift in a larger direction. The emission intensity on C-dots of lemon is thought to be greater than that of C-dots of red radish, so that the QY value of C-dots of lemon is greater than QY C-dots of red radish. This was caused by the difference in the synthesis time of C-dots lemon, which was longer than that of red radish C-dots, so that the carbonization process was more complete and more C-dots were formed.

Based on a literature study, the synthesis of C-dots from natural dyes using the solvothermal and hydrothermal methods produced C-dots with better quality than the synthesis using pyrolysis, microwave, and ultrasonic methods. The best quality of C-dots was obtained from the natural coloring compound of tannins by solvothermal and hydrothermal methods. Tannins contain many carbon atoms which function as the main precursors of C-dots, as well as oxygen which can increase the degree of surface oxidation of C-dots so that it will improve the quality of C-dots fluorescence emission. In addition to containing active tannin compounds,

precursors containing certain compounds with heteroatoms can be used as C-dots doping, such as nitrogen, sulfur, boron, and phosphorus (Yan et al. 2019). The heteroatom doping will improve the quality of the resulting C-dots emission.

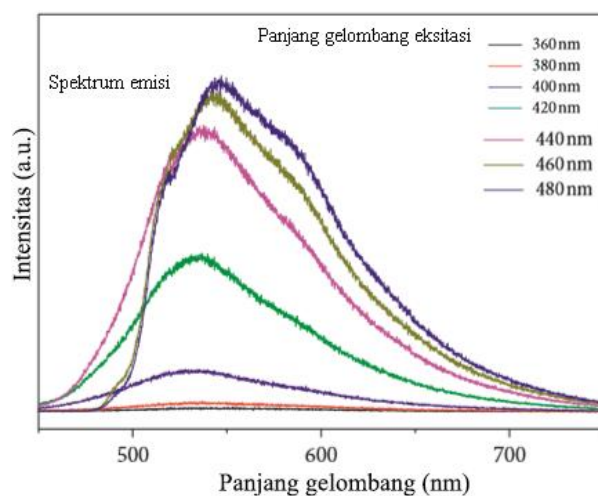


Figure 10 Photoluminescence emission spectrum on C-dots of lemon synthesized at 150 °C (Hoan et al. 2019)

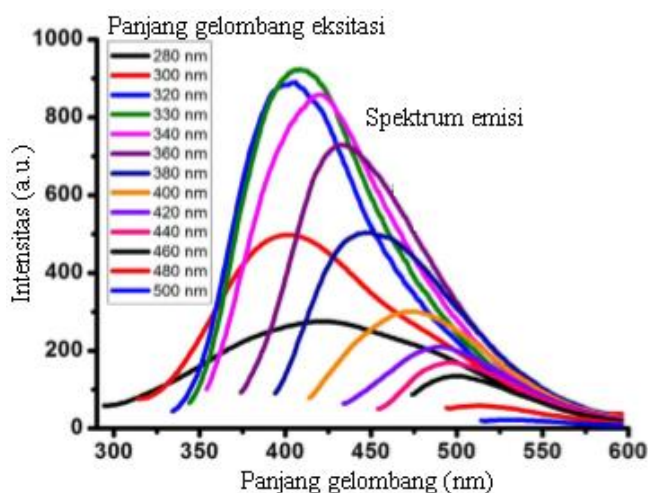


Figure 11 C-dots photoluminescence emission spectra of red radish (Liu et al. 2017)

Based on the referenced literature, the synthesis of C-dots from lemons can use the solvothermal method at a temperature of 190 °C for 10 hours with ethanol as a solvent (Ding et al. 2017), while the hydrothermal method uses 4 variations of temperature, namely 150, 200, 240, and 280 °C for 12 hours (Hoan et al. 2019). C-dots hydrothermal method used in the discussion of this subsection is C-dots which has a treatment that is almost similar to the solvothermal method, namely treatment at a temperature of 200 °C for 12 hours. The QY of C-dots using the solvothermal method is 28%, while the C-dots using the hydrothermal method produces a QY of 16.87%. Based on these data, the QY difference between the two is quite significant. The precursors used in the synthesis are the same, but have differences in solvents. In addition, the time and temperature used are almost the same.

The FTIR spectrum of the solvothermal method shows the presence of C-H, C=C, C-N, N-H, CO-OH, and C-O bonds, as shown in Figure 7a. The bonds contained in the hydrothermal C-dots are shown in Figure 8, namely the presence of CO-OH, C=O, C-H, and C-O-C bonds. The same bond is CO-OH and C-H, which is thought to come from lemons mainly from tannin compounds or citric acid. Solvothermal C-dots C=C, C-N, N-H, and C-O bonds are thought to originate from lemons whose functional group formation was facilitated by ethanol as a solvent in the synthesis process. Solvents with lower polarity and hydrophilicity will more easily

facilitate the formation of nitrogen fluorophores (Zhang et al. 2017). The C=O and C-O-C bonds formed in the hydrothermal method are thought to originate from tannin compounds which are rich in these functional groups. Tannin compounds in the hydrothermal method undergo more perfect carbonization than the solvothermal method. This is due to the higher temperature and time treatment than the solvothermal method so as to produce these functional groups. Differences in solvent, time, and temperature in the carbonization process will result in different processes occurring in the synthesis of C-dots, so that C-dots with the same precursor will produce significantly different bonds.

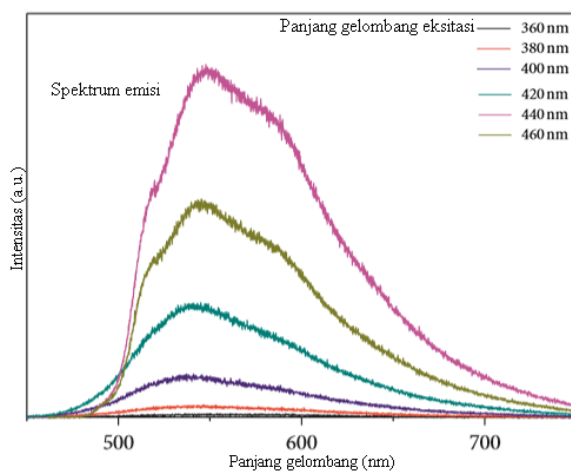


Figure 12 C-dots photoluminescence emission spectrum from lemon synthesized by hydrothermal method at 200 °C (Hoan et al. 2019)

Emissions produced by solvothermal C-dots range from 600–700 nm in wavelength, with an excitation wavelength of 440–600 nm. The resulting emission has a wavelength that is almost similar to one another. The maximum emission wavelength is at 650 nm which has an excitation wavelength of 540 nm, as shown in Figure 7a. Hydrothermal C-dots emit emission at a wavelength of 500–600 nm, with excitation at a wavelength of 360–460 nm. The emission wavelengths in hydrothermal C-dots are also almost similar to each other. The maximum emission wavelength is at 550 nm and the excitation occurs at 440 nm, as shown in Figure 12. Based on these data, the two C-dots experience a redshift, as the emission wavelength shifts in a larger direction. A larger emission wavelength is produced by solvothermal C-dots with ethanol as solvent. The solvent controls the dehydration process and the carbonization of the precursor which causes the formation of conjugated domains of various sizes in the C-dot which causes a decrease in the band gap, so that the resulting emission shifts from blue emission to red emission with a larger wavelength (Yan et al. .2019). This is also supported by the formation of the amine functional group on the solvothermal C-dots. Synthesis of C-dots with the solvothermal method produces a large wavelength or produces red emissions compared to the hydrothermal method.

## CONCLUSION

Synthesis of C-dots from tannin natural coloring compounds resulted in C-dots with QY quality and higher emission wavelengths compared to other natural coloring compounds. Precursor C-dots of natural dyes supported by other compounds that have heteroatoms can improve the quality of C-dots because it causes heteroatom doping.

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