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Green Synthesis of Carbon Dots from Nephelium Lappaceum Peels for Fluorescent Bioimaging Applications

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Abstract

In this study, the carbon dots (CDs) with diameters of less than 12 nm were successfully synthesized from Rambutan (Nephelium lappaceum) peels with the simple and green method of microwave assisted. The chemical and optical properties of CDs were investigated by Fourier-transform infrared spectroscopy (FITR) and Ultraviolet-visible (UV-vis) spectroscopy, respectively. Finally, the qualitative fluorescent property of CDs was demonstrated with optical microscopy in fluorescent modes. These are the evidence that our as-synthesized CDs have potential in fluorescent bioimaging applications.

Keywords: Carbon dots, Microwave-Assisted, Fluorescent Bioimaging

1. Introduction

Carbon dots are the relatively new nanomaterial that was first discovered in 2004 during the purification of Single-Walled Carbon Nanotube (SWCNTs) with a preparative electrophoretic method by Xu *et al.* (1). Carbon dots have gained more attention due to their comparable optical and photoluminescence properties to the conventional semiconductor quantum dots but more environmentally friendly and biocompatibility (2). In addition, carbon dot can be synthesized from S various methods such as microwave-assisted (3), hydrothermal, hydrolysis (4), and more (5). Moreover, since carbon is the main component of carbon dot, its precursors can be derived from numerous carbon sources that are easily accessible around us. One of the potential sources of carbon dot is fruit peels which consider being a low-cost food wasted thanks to the development of modern food industries to meet the demand of the change in diet habits and rising population (6). There have been many reports on the successful synthesis of carbon dots from many types of fruit peels such as orange (7), banana (8), kiwi (9), dragon fruit ,and pear (10). These fruit peels-derived carbon dot shows great potential as efficient catalysts (7) Vivo bioimaging (8) fluorescent sensor (9), and nonlinear optical applications (11). The main purpose of this work is to confirm the potential in fluorescent bioimaging applications of the carbon derived from rambutan (Nephelium Lappaceum) peels via microwave-assisted method. The Rambutan peel was chosen for this study because it is one of the food waste expected from the processed fruit industry in Thailand.

2. Materials and Experiment

The peels were collected from the Rambutans harvested in Rayong Province Thailand. The peels were rinsed in tap water and then oven dried at 100 ºC (Binder) while monitoring the weight of the three representative pieces of peels regularly until the weight of the

three reference pieces was constant. The oven-dried peels were then stored for used later.

To synthesize the carbon dot, ~5g of oven-dried rambutan peels were soaked in ~50 ml of DI water for at least 5 minutes. Then it was blended with the commercial blender (Philips 600W) until smooth. The blended mixture was then filtered through a kitchen fine mesh strainer (mesh size ~0.83mm). The 10 ml filtrate was poured into a 1000 ml beaker for microwave radiation. The microwave source is a commercial microwave oven (Electrolux). The filtrate was exposed to an 800-watt microwave for ~1 mins and then raise for ~ 30 seconds. This process was repeated until all the moisture was evaporated, and the brown residual was left at the bottom of the beaker. Then ~20 ml of DI water was poured into the beaker. The beaker was then shaken in a swirling motion to dissolve the brown residual at the bottom of the beaker. The dissolve liquid was then centrifuge (PLC-012E from Gemmy Industrial Corp) at ~ 5,000-10,000 rmp for at least 15 minutes. The Supernatant (Typically yielded ~14±2 ml) which is the carbon dot solution was mostly used for measurements right away. If not, it was stored at 4 ºC.

The as-synthesis carbon dot solution was used for UV-vis spectroscopy (Shimadzu UV-1800). To perform the FTIR (Thermo Scientific ATR Model: Nicolet iS5-iD7) investigation the carbon dot solution was first freeze-dried (Scanvac coolsafe) into a powder form (yielded ~0.6±0.1g of carbon dot powder from ~14±2 ml of carbon dot solution). The freeze-dried carbon dot is preferred for FTIR measurement because the water in the carbon dot solution may overwhelm the FTIR signal of the carbon dot with O-H peak. The TEM analysis was performed with Transmission Electron Microscope (JEM-2100Plus from JEOL) with 200 kV electron beam energy. The fluorescent imaging was performed by Optical Microscope (Zeiss).

3. Results and Discussion

3.1 Transmission Electron Microscopy (TEM)

Figure 1 a) shows a TEM image of a typical carbon dot obtained from microwave-assisted method. The shape of the carbon dot is an ellipse with the longest diameter of ~11.09 nm and the shortest diameter of ~8.21nm. The average of four diameters measured in a different direction is 9.49±1.22 nm. In Figure 1 b), the fast Fourier transform (FFT) image of the TEM shows a six-fold symmetry. The lattice space is estimated to be ~0.29±0.04 nm. The lattice space estimation and angle for all six spots on the FFT images are presented in Table 1.

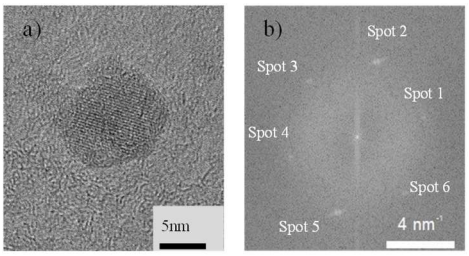

Figure 1 a) TEM image of carbon dot synthesized from Rambutan (Nephelium lappaceum) peels via microwave-assisted. b) fast Fourier transform (FFT) image of carbon dot contained six bright spots.

Table 1 Lattice spaces (r) and angles estimation of fast fourier transform image of carbon dot.

Spots	r (c/nm)	Angle (degree)
1	0.29±0.1	15.9±0.5
2	0.29±0.1	73.2±0.5
3	0.29±0.1	133.6±0.5
4	0.29±0.1	195.4±0.5
5	0.29±0.1	254.3±0.5
6	0.29±0.1	314.3±0.5

The size of the carbon dot and atomic lattice space in this study is comparable and larger than the carbon dot derived from different types of fruit peels in previous studies. Prasannan and Imae reported their hydrothermal synthesized carbon dot from orange peels to have a size range from 2-7 nm (7). Atchudan *et al.* synthesized carbon dots from banana peels with the particle size of 4-6 nm with an atomic lattice space of 2.1 nm (8). In a separate study, Atchudan et al. achieved a 3.0-9.0 nm with 0.21 nm lattice separation from kiwi peel via the hydrothermal method (9). To the best of our knowledge, there is no report of the size measurement using TEM of carbon dot from fruit peels synthesized via microwave-assisted method. The reason for the larger dimension and lattice space of our carbon dot may arise from the synthesis method of microwave-assisted with fruit peels.

3.2 UV-visible Spectroscopy

Figure 2 shows the UV-vis result of carbon dot solution after a dilution to prevent the overload signal. There is two absorption shoulders center at 252±1 nm and 353±1 nm. These two shoulders are likely related to $\pi - \pi *$ transition of C=C bonds and $n - \pi *$ transition of C=O, respectively (12). Similarly, these two transitions were also observed carbon dot derived from other fruit peels. In comparison, the absorption of $\pi - \pi *$ transition was observed at ~268 nm, 277 nm, and 275 nm for carbon dots synthesize from orange peels (7), banana peels (8), and kiwi peels (9), respectively. As for the $n - \pi *$ transition, there were reports of the absorption peak at 322nm, 327nm of carbon dot derived from banana peels (8) and kiwi peels (9), respectively. This result indicates that there is a slightly larger $\pi - \pi *$ energy gap and smaller $n - \pi *$ of our carbon dot from rambutan peels when compares to other previous studies. The difference in molecular electronics structure between our carbon dot and previous studies' can arise from either the difference in synthesis method (microwave-assisted for this study and hydrothermal for (7)(8)(9)). Another reason can be that the different electronic structure arises from the different chemical components of each fruit peels as a carbon precursor.

3.3 FTIR

To investigate the functional group of carbon dot, the FTIR was performed on a freeze-dried carbon dot solution. Figure 3 depicts The FTIR result. The absorption bands are observed at 1043±1, 1207±1, 1338±1, 1608±1, 1697±1, 2972±1, and 3267±1 cm^{-1}. The band at 1043±1 cm^{-1} is corresponding to a C-O bond of hemicellulose (13). The peak originated from C-O ether group from either lignin or cellulose (14). The band at 1608±1 cm^{-1} is from C=C stretching of aromatic skeletal mode. The peak at 1697±1 cm^{-1} is from C=O stretching of ketone (15). A peak at 2972±1 cm^{-1} is from aliphatic C-H group stretch mode and A peak at 3267±1 cm^{-1} is from O-H stretching mode (16). Oliveira *et. al.* reported in their study that the main components of their rambutan peel fiber are lignin, cellulose, and hemicellulose, respectively (13). As a result, our as synthesized carbon dot may have inherited some chemical properties from these main components.

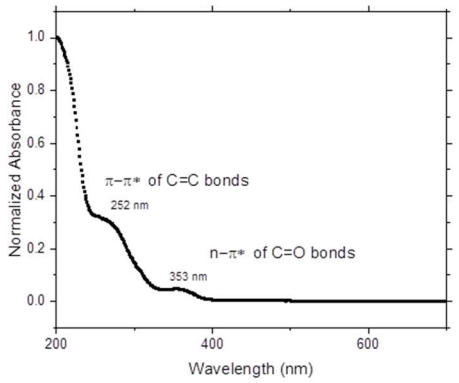

Figure 2 Normalized Uv-vis Spectrum of as-synthesized carbon dot solution synthesized from Rambutan (Nephelium lappaceum) peels via microwave-assisted.

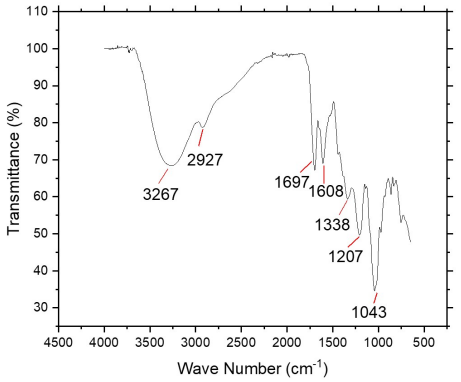

Figure 3 FTIR Transmittance Spectrum of carbon dot solution synthesized from Rambutan (Nephelium lappaceum) peels via microwave-assisted.

3.4 Fluorescent Imaging

The potential application of carbon dot as a fluorescent dye was qualitatively demonstrated by comparing the optical images of the white part of spring onion (Allium fistulosum) that were soaked in as-synthesized carbon dot solutions (Figure 4) and DI water (Figure 5). The soaking time is about five minutes. In the optimized setting for fluorescent images, the image from the tissue that was soaked in carbon dot solution is brighter than the image from the tissue that was soaked in DI water. For the sample soaked in carbon dot solution, the images in the fluorescent mode for Texas red, FITC, and DAPI fluorescent mode depicted better features of the cell wall when

compared to the images of the sample soaked in DI water in their respective fluorescent modes with the same settings. This is evidence that the white part of the spring onion showed almost no autofluorescence under our imaging condition. According to Donaldson, the two most studied auto fluorescent in plants are chlorophyll and lignin (17). In the white part of the onion, we expected less chlorophyll and no lignin. Although there could be other molecules with autofluorescence properties in the white part of the spring onion, the amounts are likely too small for its autofluorescence to be observed in our study (Figure 5 b)-c)). Note that, the as-synthesized carbon dot solution used for fluorescent imaging in this study was not yet modified to enhance it properties.

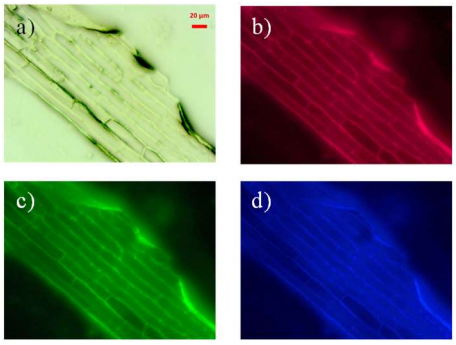

Figure 4 Optical Images of spring onion (Allium fistulosum) soaked in carbon dot solution in a) bright field mode, b) Texas red mode, c) FITC mode, and d) DAPI mode, respectively

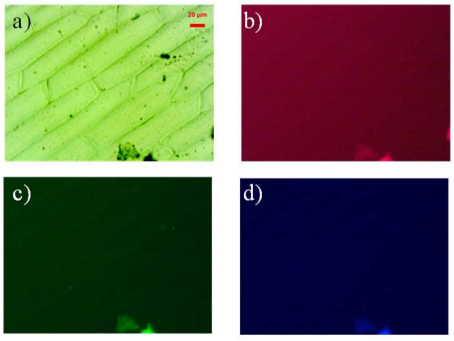

Figure 5 Optical Images of spring onion (Allium fistulosum) soaked in DI water in a) bright field mode, b) Texas red mode, c) FITC mode, and d) DAPI mode, respectively

4. Conclusions

In this study, the carbon dot was prepared by a simple and green method of microwave-assisted with could easily achieve by a typical household microwave oven. With this simple method, one can achieve the carbon dot with comparable properties to the fruit peels derived carbon dot from previous studies. The diameter and the atomic lattice space of the carbon dot in this work are slightly larger than the prior work but are still in the same order of magnitude. The UV-vis result indicates a similar electronic structure with slightly different energy values when compared to the carbon dot from other studies. The FTIR result of the carbon dot from rambutan peels is slightly different from the result of carbon dots derived from other fruit peels. This is to be expected due to the different chemical compositions unique to the peels of each type of fruit. Finally, the rambutan peels carbon dot shows better fluorescent properties than DI water in fluorescent imaging. Although at its current state, our carbon dot is still far from practical usage in bioimaging application we believe it has potential worth for further research.

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Declaration of conflicting interests

The authors declared that they have no conflicts of interest in the research, authorship, and this article's publication.

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