Photoluminescence study of carbon dots from ginger and galangal herbs using microwave technique

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Abstract. Carbon dots are new type of fluorescent nanoparticle that can be synthesis easily from natural sources. We have synthesized carbon dots from ginger and galangal herbs using microwave technique and studied their optical properties. We synthesized colloidal carbon dots in water solvent by varying microwave processing time. UV-Vis absorbance, photoluminescence, time-resolved photoluminescence, and transmission electron microscope were utilized to study properties of carbon dots. We found that microwave processing time significantly affect optical properties of synthesized carbon dots. UV-Vis absorbance spectra and time-resolved photoluminescence results show that luminescence of carbon dots is dominated by recombination process from n–π* surface energy level. With further development, these carbon dots are potential for several applications.

1. Introduction
Carbon dots are newly discovered carbon-based nanostructure in last decade [1, 2]. Carbon dots differ from other carbon-based nanostructure, such as graphene dots, carbon nanotubes, etc. Carbon dots are solid spherical carbon nanostructures, which have good optical properties [2 – 4]. Carbon dots have good optical stability and moderate luminescent efficiency so that they can be utilized for various optical devices such as light emitting diodes and solar cells [3 – 5]. Carbon dots are also can be applied as photo-catalyst and bio and chemical sensors. Synthesis of carbon dots is also relatively simple. Several simple techniques, such as hydrothermal, solvothermal, ultrasonic, and microwave techniques have been demonstrated to produce carbon dots [1, 6]. Those techniques have shown simple and fast synthesis process of carbon dots. The interesting fact regarding carbon dot synthesis is that most of natural resources can be utilized as the carbon sources. Many researchers have shown that carbon dots can be synthesized from sugar, leaves, fruit peels, beverages, and many more [7, 8]. In addition, some researchers also employed high purity chemicals, such as oleic acid, to fabricate carbon dots [9]. However the optical properties of carbon dots prepared either from natural resources or high purity chemicals are comparable. Therefore, the utilization of natural resources for synthesizing carbon dots becomes an advantage for carbon dots research. The utilization of natural resources to produces luminescent carbon dots can reduce pollution in air, water, and soil; therefore, this technology becomes environmental friendly.
In this work, we focused on synthesis of carbon dot from herbs, i.e., ginger and galangal. Ginger and galangal are herbs that are commonly found in tropical countries. They have strong flavor and have been utilized as spices for cooking or healthy drinks. In this work, synthesis of carbon dots from ginger and galangal was done using microwave technique which was chosen due to its simplicity. Many researches previously have shown that microwave technique can easily synthesize carbon dots [1, 5]. However, in their articles, there was no information regarding the influence of microwave processing time on optical properties of synthesized carbon dots. The purpose of this work is to synthesize and optically characterize carbon dots made of ginger and galangal using microwave technique with different microwave processing time.

2. Sample preparation and measurements
The synthesis procedure of carbon dots from of ginger and galangal herbs using microwave technique is shown in figure 1. Each herb was crushed using domestic electrical blender in water. The blended herb was then filtered to get extract solution and then placed in a 450 W domestic microwave oven. Microwave processing time was varied from 5, 10, 20, and 40 minutes until brown dried sample was obtained. After that, the sample was dissolved and centrifuged to separate the brown liquid and precipitate. Final brown liquid which contains colloidal carbon dots, was then characterized using transmission electron microscope (TEM FEI Tecnai 200 kV), UV-Vis absorbance, photoluminescence (PL) and time-resolved photoluminescence (TRPL). We measured absorbance using deuterium and halogen lamps as light source and MAYAPRO2000 from Ocean Optics as photospectrometer. PL and TRPL were performed using picosecond diode laser at wavelength 420 nm as excitation source.

3. Results and discussion
In general, we have successfully synthesized carbon dots from ginger and galangal herbs. There are two easy hints indicating the presence of carbon dots, i.e. brown color solution and light emitted from solution upon blue laser excitation as shown in figure 2. The brown color solution indicates that carbon dots perfectly dissolved in water solvent. After few weeks, we did not notice any sedimentation from sample indicated that carbon dots and water solvent are a stable colloid. The light emission coming from carbon dots colloid solution is mostly cyan color or light-green. However, not all of the samples give good indication of carbon dots existence. As shown in table 1, sample with 5 minutes...
microwave processing time from galangal herb does not show brown color and light-green emission color. We notice that increasing microwave processing time will increase number of synthesized carbon dots indicated by darker brown color.

Figure 2. Appearance of colloidal carbon dots under (a) ambient illumination, (b) blue laser illumination, and (c) its TEM images.

Table 1. A slightly more complex table with a narrow caption.

| Sample number | Original source | Microwave processing time (minutes) | Appearance color |
|---------------|----------------|-------------------------------------|-----------------|
| 1             | Ginger         | 5                                   | Brownish white  |
| 2             | Ginger         | 10                                  | Light Brown     |
| 3             | Ginger         | 20                                  | Brown           |
| 4             | Ginger         | 40                                  | Dark brown      |
| 5             | Ginger         | 5                                   | Milky white     |
| 6             | Ginger         | 10                                  | Brownish white  |
| 7             | Ginger         | 20                                  | Light brown     |
| 8             | Ginger         | 40                                  | Brown           |

In order to confirm our carbon dots, we conducted TEM measurement as show in figure 2c. We could not obtain clear TEM image due to small size of carbon dots. However, from TEM image, we can confirm that small size of carbon dots exist in the sample. We predicted that size of carbon dots below 10 nm, which is typical size of carbon dots [1, 10,11].

In order to study optical properties of carbon dots, first we measured absorbance of colloidal carbon dots. We only measured 7 samples from table 1. Sample number 5 did not show any absorbance peak. For all measured samples, we observed that there are two clear absorbance peak, i.e., at 270 nm wavelength and 370 nm wavelength. Absorbance peak around 270 nm wavelength is related to $\pi-\pi^*$ energy level from core of carbon dots, and absorbance peak around 370 nm wavelength is related to $n-\pi^*$ energy level from surface of carbon dots [10,11]. For further analysis in this work, we focused on energy level from surface of carbon dots. After normalization of absorbance spectra (as shown in figure 3), we notice that absorbance value at wavelength around 370 nm wavelength increases as microwave processing time increases (as shown in the inset figures of figure 3). For carbon dots made of ginger, the absorbance value at 370 nm wavelength linearly increases as microwave time increases. However, a little bit different trend was observed for carbon dots made of galangal. The increase of absorbance value at 370 nm wavelength indicates that the role of surface energy level increases in carbon dots.

Luminescent of carbon dots were obtained using photoluminescence experiment as shown in figure 4. For colloidal carbon dots made of ginger (figure 4a), we found that carbon dots with microwave processing time up to 20 minutes show similar luminescent spectra and peak position. Carbon dots with 40 minutes processing time shows different luminescent spectrum. The spectrum is red shift, which is shifted to longer wavelength. In addition, the luminescent spectra of carbon dots made of
galangal show similar trend (figure 4b). Carbon dots with 5 minutes microwave processing time did not give any luminescent upon blue laser excitation. The emission occurs from carbon dots with 10 minutes microwave processing time. Luminescent spectra from carbon dots with longer microwave shift to longer wavelength. Comparison of carbon dots luminescent spectra from ginger and galangal (figure 4c and d) shows the luminescent spectra become identical after 40 minutes microwave processing time. We believe that 40 minutes microwave processing time to be the optimum condition for synthesizing carbon dots.

In addition to photoluminescence, we also observed exciton decay time from every sample of carbon dots using TRPL measurement as shown in figure 5. For carbon dots made from ginger (figure 5a) and carbon dots made from galangal (figure 5b), we found that microwave processing time affects exciton decay time. Longer microwave processing time gives shorter excitation decay time (as shown in figure 4.d). This indicates that luminescent of carbon dots is dominated from n-$\pi^*$ (surface) energy
level as predicted by earlier. We also found that, although luminescent spectra of carbon dot made from both ginger and galangal (figure 4d) are similar, but the exciton decay time of carbon dots made from ginger is much shorter than those from galangal.

![Figure 5. Time-resolved photoluminescence spectra of colloidal carbon dots made from (a) ginger and (b) galangal, and (c, d) their comparison.](image)

4. Summary
We have successfully synthesized carbon dots from ginger and galangal herbs. Green color luminescent was obtained from every carbon dots sample. We found that microwave processing time significantly affected optical properties of synthesized carbon dots. For both samples (ginger and galangal), 40 minutes microwave time gives almost similar optical properties, especially photoluminescence spectra. UV-Vis absorbance spectra and time-resolved photoluminescence results show that luminescent of carbon dots is dominated by recombination process from \( n-\pi^* \) (surface) energy level.

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