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Optical properties comparison of carbon nanodots synthesized from commercial granulated sugar using hydrothermal method and microwave

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Abstract

Optical properties comparisons of carbon nanodots (C-dots) from commercial granulated sugar via hydrothermal method and microwave have been conducted. The granulated sugar mass is varied, i.e.: (in grams) 10, 20, and 40, each dissolved into 250 ml of distilled water. The hydrothermal method is performed by heating the sugar solution in an autoclave inside an oven for 5 h at 150 °C, while the microwave technique is done by heating the sugar solution inside a microwave oven for 40 min. The resulting colours of the C-dots solutions using the hydrothermal method and microwave are light to dark brown and yellow to dark brown, respectively. The C-dots are characterized using UV—vis, PL, TRPL, and FTIR spectroscopies, and also TEM. The general optical properties of the C-dots obtained from both synthesis are similar, but different in the details. These general optical features of the C-dots are brownish colored solutions, green luminescence, and spherical shaped particles. The differences of the C-dots from the microwave technique compared to the hydrothermal method include: a shorter UV—vis wavelength at maximum absorbance values of the core, broader PL wavelength at the emission peaks, faster emission time of TRPL, and smaller diameter size of the particles.

1. Introduction

A nanomaterial that is being and continues to be studied is carbon nanodots (*C*-dots). *C*-dots are a new class of carbon nanomaterial with sizes below 10 nm, which is first obtained from the purification of single-walled carbon nanotubes through preparative electrophoresis in 2004 [1]. *C*-dots have some advantages, including low toxicity, no heavy metals, strong photoluminescence, and abundant of raw carbon materials in nature. The latter advantage triggers various *C*-dots studies based on a variety of materials such as, soy milk [2], orange juice [3], and citric acid [4]. *C*-dots utilize the carbon contained in the aforementioned materials to produce high-performance nano-sized carbon particles in technological advancements, such as white LEDs [5], bio-labeling and imaging [6, 7], and metal-ion sensing [8].

C-dots can be synthesized via a variety of methods, which are generally classified into top-down and bottomup methods [9]. The former is a physics-based method, which includes laser ablation, arc discharge, and plasma treatment, while the latter is a chemical method that includes electrochemistry, hydrothermal, microwave, and support assisted synthesis [10]. In the top-down method larger carbon bonding structures are broken down to form C-dots particles whereas in the bottom-up method the formation of C-dots are derived from a precursor molecule [9].

The microwave method is conducted by direct heating process of the (raw) materials inside a microwave oven, which may simplify and accelerate the synthesis process of C-dots [11]. Another method involving heating process is the hydrothermal method, which is categorized as a simple method because the principle of heating uses low oxygen content [12]. Various studies have synthesized C-dots using microwave and hydrothermal

methods based on natural materials. Zhu, $et\,al\,(2009)$ in [13] synthesizes C-dots using the microwave method with heating time within minutes. The saccharides, e.g. glucose and fructose, are dissolved in water and then heated in a 500 W microwave oven for 2 to 10 min. The color changes from colorless to yellow to light brown indicate the formation of C-dots. Liu, $et\,al\,(2011)$ in [8] synthesizes C-dots from wax soot with hydrothermal reaction. The collected wax soot is sonicated in NaOH solution and heated at 200 °C in a sealed container in a polytetrafluoroethylene reaction. The product is cooled and centrifuged giving a brown-yellow supernatant, and then neutralized with HCl, and followed by dialysis.

In this study, we compare the optical properties of the C-dots produced from commercial granulated sugar based on microwave technique and hydrothermal method. We use the aforementioned methods because the two methods are given the same treatment, that is heating, but with different preparation and heating processes. This may be important in the application of C-dots for certain purposes that depends upon the synthesis method. In general, it is commonly accepted that different ways of synthesizing nanomaterials produce different physical and chemical characteristics of the nanomaterials. Hence, differentiating the optical properties of the C-dots resulted from similar heating techniques may help in determining the appropriate method in synthesizing C-dots especially for optical applications.

The natural ingredient used in this study is commercial granulated sugar because of its large availability in the market as well as the amount of carbon content in it, especially sucrose. Sucrose is a disaccharide that consists of one molecule glucose and one molecule fructose [14]. In this case, we acknowledge that glucose has been a precursor for producing luminescent C-dots, e.g.: see [15–17]. However, the study of glucose-based materials, such as cow menure [17], for the production of C-dots are still being carried out, including in this case from granulated sugar [18]. In this study we go further by comparing the optical properties of C-dots from commercial granulated sugar produced via the hydrothermal method and microwave-assisted technique. To the best of our knowledge, this study has not been conducted before and hence contributes to the various literatures of glucose-based materials as precursor for producing C-dots. The comparison of the optical properties is conducted via UV-vis spectroscopy, photoluminescence (PL), time-resolved photoluminescence (TRPL), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR).

2. Experimental methods

The preparation of granulated sugar solution as a stock solution is made by dissolving 10 grams of granulated sugar into 250 ml of distilled water. The solution is then stirred using a magnetic stirrer for 15 min. Finally, the sugar solution is transferred into a bottle as a stock solution. The same steps are carried out for 20 and 40 grams of sugar, each dissolved into 250 ml of distilled water. The solutions of 10, 20, and 40 grams of sugar, each in 250 ml distilled water, are referred to as sample 1, 2, and 3, respectively.

The synthesis of C-dots via the microwave for sample 1, 2, and 3 is conducted separately, but with the same steps. Each sample is poured into a 50 ml beaker glass and then put into a microwave oven for 40 min. The resulting sample is the crusts on the bottom of a beaker glass. The crusts are cooled and then 100 ml of distilled water is added. The sample is shaken until it is evenly mixed and leaves no residue. The solution is inserted into a small bottle for centrifugation for 30 min in order to separate the C-dots solution with the precipitate. The resulting precipitate is at the bottom of the bottle while the C-dots solution is above it. Finally, the C-dots solution is separated from the precipitate.

The synthesis of C-dots via the hydrothermal method for sample 1, 2, and 3 is performed separately, but also with the same steps. 30 ml of each sample is poured into an autoclave and heated in an oven for 5 h at 150 $^{\circ}$ C. Then the autoclave is removed from the oven and left alone for approximately 16 h for the cooling process. The resulting sample is the C-dots solution. The C-dots solution is inserted into a small bottle for centrifugation for 30 min in order to separate the solution of C-dots with the precipitate. Finally, separation between the C-dots solution and the precipitate is conducted.

The UV–vis, PL, and TRPL characterizations to determine the absorbance, luminescence emission, and luminescence emission time of the C-dots solution, respectively, are conducted using Spectrometer MayP112615 spectrum 2068. The laser used is at an excitation wavelength of 405 nm. The FTIR characterization to identify functional groups produced by C-dots solution is done using Thermo Scientific Series Nicolet iS10 Smart iTR 500–4000. Finally, TEM images to study the surface morphology and diameter size of C-dots are obtained from the TEM test apparatus.

3. Results and discussion

The synthesis of C-dots from commercial granulated sugar by hydrothermal method yields solution colours from light brown to dark brown as the mass of the sugar is increased, as shown in figure 1(a). Moreover, the

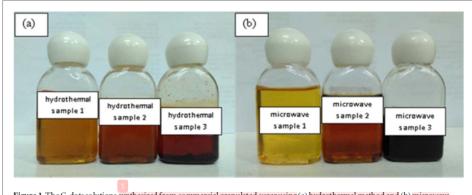
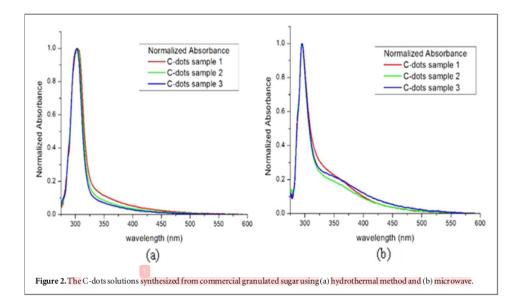


Figure 1. The C-dots solutions synthesized from commercial granulated sugar using (a) hydrothermal method and (b) microwave.

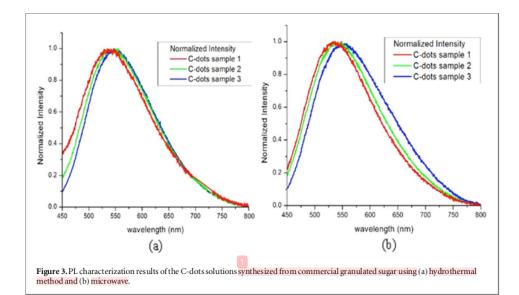


synthesis of C-dots by microwave yields solution colours from yellow to brown as seen in figure 1(b). The color changes indicate that as the mass of the sugar is increased the resulting color of the solution becomes darker. This is expected as the mass of the sugar is increased, the concentration of the C-dots produced increases, and hence the solutions become murkier. A sharp color contrast is clearly seen from the C-dots via the microwave compared to the hydrothermal method. All samples from the hydrothermal method are brownish in colour. However, the C-dots samples from the microwave method changes from yellow, brown, to dark colour.

The synthesis results of the C-dots solutions from commercial granulated sugar based on the two methods are then characterized using UV-vis, PL, and TRPL spectroscopies. UV-vis characterization is performed to determine the absorption pattern of the solutions at a certain wavelength interval of 200 nm to 600 nm. The characterization results of the C-dots solutions for the two methods are shown in figure 2.

The absorption patterns of the three samples from the hydrothermal method (figure 2(a)) produce one absorption peak at a wavelength of 303 nm. The absorption peak at that wavelength indicates that the electrons undergo transition from $\pi \to \pi^*$ (core). Furthermore, the absorption patterns form for the three samples from the microwave (figure 2(b)) have two absorption peaks. The first peak for all three samples is at the same wavelength of 295 nm. The second peak for sample 1, 2, and 3 occurs at a wavelength of 356 nm, 363 nm, and 369 nm, respectively. The first absorption peak indicates again electronic transitions of $\pi \to \pi^*$ (core), whereas the second absorption peak indicates electron transitions of $n \to \pi^*$ (surface state).

The UV-vis graphs from the hydrothermal method have a smooth shape and no peak appears on the tail. It may be observed that the surface state of the UV-vis data from the hydrothermal method does not appear.



However, the peak of the surface states should still be present, hence suggesting that the peak of the surface states is not readable from the apparatus in figure 2(a). The absence of the surface state peak of the C-dots by hydrothermal method could be caused by the absence of a passivation agent in accordance with the study conducted by Peng, $et\,al\,(2009)$ in [19]. The UV—vis graphs of the C-dots from the microwave technique seem to have narrower peaks compared to the hydrothermal method. This may explain the colour contrast of the C-dots solutions from the microwave technique, which is better than the hydrothermal method. Moreover, the wavelength of the first peak (core) from the hydrothermal method and microwave is not that different, although it is shorter for the microwave method, i.e.: 303 nm compared to 295 nm. This suggests that the C-dots solutions

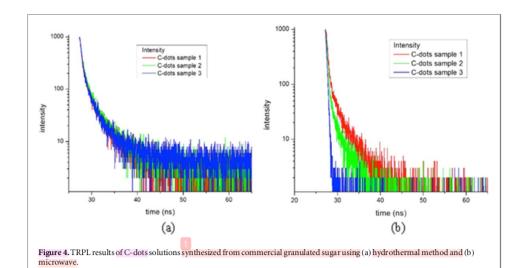
Furthermore, the PL characterization with laser excitation wavelength of 405 nm is conducted to determine the emission wavelength produced by the C-dots solutions. The results of PL characterization of the three samples for both synthesis are shown in figure 3.

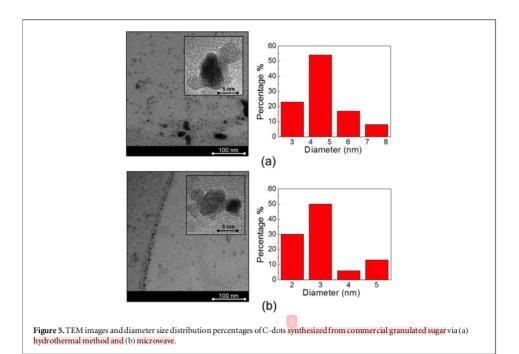
produced by hydrothermal method and microwave absorb different wavelengths of ultraviolet light.

The emission peaks of the C-dots solutions synthesized via the hydrothermal method for the three samples are located at different wavelengths. The intensity peaks of sample 1, 2, and 3 are located at a wavelength of 540 nm, 544 nm, and 548 nm, respectively. The C-dots solutions synthesized from the microwave technique also produce emission peaks at different wavelengths. The intensity peaks of sample 1, 2, and 3 are at a wavelength of 533 nm, 538 nm, and 547 nm, respectively. The luminescence color produced by the C-dots solutions obtained from both methods is green, which has a wavelength from 500 nm to 570 nm. However, the green color range of the intensity peaks is broader for the C-dots from the microwave technique compared to the hydrothermal method, that is 533 nm to 547 nm compared to 540 nm to 548 nm, respectively. It may also be observed that the peaks of the three C-dots samples from both methods progressively shift to higher wavelength, i.e. a red shift occur. This happens as the mass of the commercial granulated sugar increases. The red shift is more clearly observed for the C-dots samples synthesized from the microwave compared to the hydrothermal method.

In addition to the UV—vis and PL characterizations, TRPL characterization is performed to determine the dynamics of luminescence or emission time interval. The TRPL characterization results of the C-dots solutions from the two methods for the three samples are shown in figure 4. The graphs in figure 4, which is obtained from TRPL characterization are analyzed and fitted using exponential decay-1 function via Origin application. The results of the data fitting for the C-dots solutions from the hydrothermal method is 0.654 ns, 0.759 ns, and 0.671 ns for sample 1, 2, and 3, respectively, whereas it is 0.554 ns, 0.461 ns, and 0.399 ns for sample 1, 2, 3, respectively, for the microwave technique. In general, the emission time of electrons is longer for the C-dots synthesized from hydrothermal method compared to the microwave technique. This shows that the surface states in the C-dots by the microwave method are more dominant than in the C-dots by hydrothermal method, which is in agreement with the UV—vis data in figure 2.

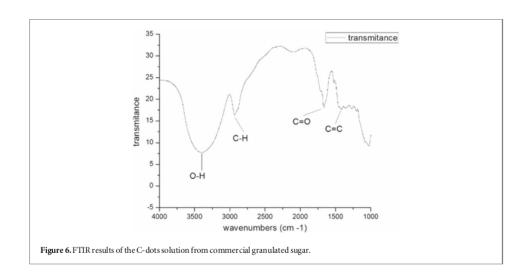
TEM is conducted to determine the morphology and diameter size of the C-dots produced by both methods. The TEM results obtained for C-dots from both methods are given in figure 5. The TEM results for the C-dots





from both methods show spherical particles distributed homogenously throughout the sample. Inset figures show clear TEM images for single or few C-dots particles, which reveal lattice structure of the C-dots. However, the distribution sizes of these C-dots are different between the hydrothermal method and the microwave technique. For the C-dots produced by hydrothermal method, the sizes of the particles are around 2.9 nm to 7.3 nm, whereas for the microwave method the sizes are around 1.9 nm to 4.8 nm. This clearly shows that the C-dots synthesized from the microwave method produce smaller size particles.

Finally, to determine the functional groups of the C-dots from commercial granulated sugar, the FTIR characterization is performed. This may be observed in figure 6. The functional groups formed in the C-dots solution from granulated sugar are [20] OH at 3400 cm⁻¹, C-H at 2931 cm⁻¹, C=O at 1666 cm⁻¹, and C=C at 1420 cm⁻¹. The FTIR results show that the C-dots solutions are successfully synthesized from commercial



granulated sugar with the presence of C=C functional group that makes up the core part of the C-dots, while OH, CH, and C=O make up the surface states.

The characterizations above point to a general finding that the optical properties of the C-dots produced by hydrothermal method and microwave technique are quite similar in the general (averaged) features, but different in the details. The color of the resulted C-dots solutions from both methods is brownish color however the color (contrast) details are different as the mass of the sugar is increased. The UV-vis results show that the C-dots from both methods have a $\pi \to \pi^*$ transition peak averaged at 299 nm, but the peak is at a shorter wavelength for the microwave compared to the hydrothermal method. Moreover, the UV-vis graphs of the C-dots from the microwave seem to be narrower compared to the hydrothermal method. The PL characterization finds that the luminescence colour of the C-dots from both methods is green, however, the details of the PL spectrums of the C-dots from the two methods are different, i.e. broader emission peak is obtained for the microwave method. Finally, the TEM images show spherical particles of C-dots from both methods, but the C-dots from the microwave method tend to have a smaller size distribution. This confirms that the synthesis method affects the optical characteristics of the C-dots obtained. Moreover, the differences in the detail characteristics of these C-dots suggest that the synthesis method of the C-dots may effect their applications for specific purposes. For example, based on the TRPL results the longer emission time of the C-dots sample from the hydrothermal method shows a better quality of the material compared to the microwave technique. Therefore, this indicates that the hydrothermal method might be preferable (compared to the microwave technique) to produce C-dots material for optical applications, such as for LEDs or bio-imaging. Of course, the TRPL is just one parameter that may be used to choose the appropriate method for synthesizing C-dots, A better way would be to consider all characterization results as more results give more information concerning the physical and chemical properties of the C-dots.

4. Conclusions

C-dots solutions are produced from commercial granulated sugar via the hydrothermal method and microwave technique. The optical properties of the C-dots from the hydrothermal and microwave methods are compared based on UV-vis, PL, and TRPL spectroscopies, TEM images, and FTIR. The general features of the C-dots obtained from hydrothermal method and microwave are quite similar however the details of the characterization results are different. The general features of the C-dots from both methods are brownish coloured solutions, green luminescence, and spherical shaped particles. The optical property differences of the C-dots from the microwave method include (i) a shorter wavelength at maximum UV-vis absorbance of the core, (ii) broader PL wavelength at the emission peaks and faster emission time of TRPL, and (iii) smaller diameter size of the C-dots particle.



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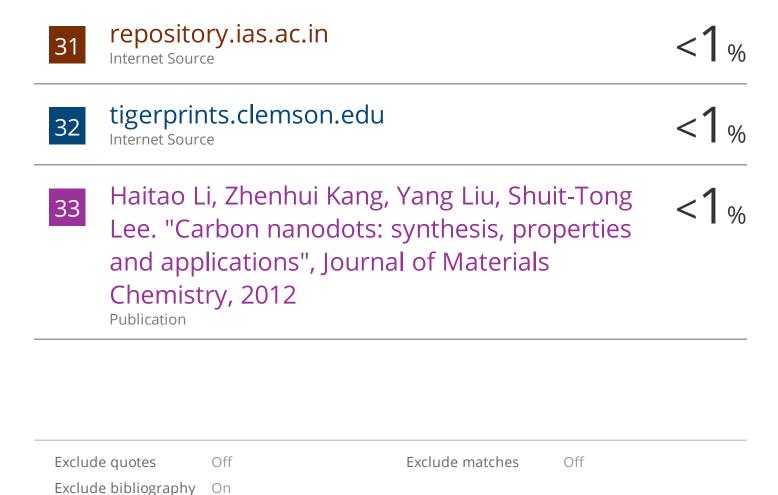
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