Preliminary Study of Heat Supply during Carbon Nanodots Synthesis by Microwave-assisted Method

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Abstract. Carbon nanodots (CNDs) are known to be good phosphor materials with wide range emission band, low cytotoxicity and excellent biocompatibility. In this work, CNDs were synthesized from a precursor consisting of citric acid [C₆H₈O₇] as carbon source and urea [(NH₂)₂CO] as nitrogen source through a microwave-assisted method. The heat energy supplied during the microwave process was controlled. Further, we studied the effect of citric acid mass on the photoluminescence (PL) properties of the CNDs by varying its percentage in the precursors. The optimum luminescence intensity was obtained from the sample that was produced from 1.2 wt% citric acid mass. It had a single emission band with bright yellow luminescence.

1. Introduction

Carbon nanodots (CNDs), an important member of the carbon family, have attracted much attention lately due to their low toxicity, excellent biocompatibility, and low cost, and the abundance of their raw materials in nature [1-4]. The size and surface of the chemical groups of CNDs may affect their fluorescent properties. Therefore, careful selection of the constituent precursor composition and synthesis method should be done.

Among the possible methods for preparing of CNDs, a microwave-assisted method is a relatively simple process with advantages over other methods [5]. Firstly, the microwave itself is a tool at an affordable price that can be easily found on the market. Secondly, microwaves are non-ionizing electromagnetic waves due to their low radiation energy and are environmentally friendly [6]. The microwave process transforms the electrical energy into heat energy. During the heating process, the microwaves are capable of penetrating very deeply into certain materials [7], therefore microwaves are suitable to be used for synthesis and modification of carbon nanostructures, including CNDs. Several researches have reported synthesis of CNDs samples in liquid phase [8-10]. Qu et al. reported a simple synthesis route of CNDs towards water-soluble using citric acid and urea as precursors [8]. Das et al. reported the optimization of synthesis green emitting CNDs by varying the concentration and solution pH of the precursors, respectively [9]. However, only a few studies with high fluorescence in solid phase have been reported [11,12]. Meanwhile, solid phase CNDs are important for commercial
application. In addition, the microwave method developed to produce CNDs in previous researches is still not able to identify sample temperature and heat energy during the heating process. Therefore, an attempt to produce solid-phase CNDs by microwave heating method is needed, along with designing a microwave oven that is able to measure sample temperature during the heating process. Here, we report an approach to precisely control of the CNDs samples by modifying a commercial microwave apparatus. This method was specifically designed to monitor the sample’s temperature during the heating process in the microwave. In order to optimize the photoluminescence properties, we studied the effect of citric acid mass by varying its percentage in the precursors and observing the phase transition of the sample during the synthesis process.

2. Experimental Procedure
CNDs were synthesized via a reaction of citric acid (CA) (Merck) with commercial urea through a microwave-assisted method. In brief, several mass variations of CA (0.015-0.250 g) and 3 g urea were dissolved in 5 ml distilled water in a beaker. Then the solution was stirred for 5 minutes and heated in an oven at 100 °C for an hour. A microwave oven with 800 W of power was activated for 2 minutes, until the colorless powder had changed into the color of visible light and a light yellow solid phase of CNDs was obtained. The synthesis process is outlined in Figure 1. Further, the photoluminescence (PL) intensity of the CNDs sample was determined by photoluminescence spectrofluorometer (PL Spectra., RF-5300PC, Shimadzu Corp., Kyoto). The device consists of a xenon laser, which emits a continuous spectrum with a wavelength of 200-800 nm.

The sample’s temperature in the microwave was controlled by introducing an infrared thermometer mounted on top of the microwave, as shown in Figure 2. The infrared thermometer was calibrated with a thermocouple in order to obtain correct temperature measurement.

Figure 1. Synthesis procedure of CNDs using microwave heating.

Figure 2. Design of a microwave with infrared thermometer.

3. Results and discussion
Figure 3 shows the relation between sample temperature and heating time with variation of CA mass between 0 and 7.7 wt%. From Figure. 3, it can be seen that the sample temperature increased during the heating process in the microwave oven. Therefore, it affected a change in the color and phase of
the sample as shown in Figure 4. Moreover, the phase transition of the sample occurred within at a certain temperature range. First, after heating at 110 °C, the sample changed into liquid phase. Once it reached 165 °C, the sample turned into semi-liquid phase. After that it turned back to solid phase. These changes indicate that the heat transfer caused a melting process during microwave heating. This confirms that the melting point of the sample was about 110 °C. On the other hand, the phase transition did not appear at heating below 100 °C due to insufficient heat energy being available for the phase transition from solid into liquid. This indicates that there is a certain amount of heat energy required to achieve balance between both chemical and physical reactions. Thus, we propose that the amount of heat energy transfer should be calculated because it has an important impact on the luminescence properties. Further investigation is needed to understand this phenomenon.

Figure 3. Graph of the relation between sample temperature and heating time With variation of CA mass (0-7.7 wt%).

Figure 4 shows the produced CND samples. After heating the samples in the microwave oven, the samples with 0 and 0.5 wt% CA had a white color, the sample with 1.2 wt% CA had yellow color, the samples with 2.5 wt% and 4.0 wt% CA, had a tawny and brown colors respectively, the sample with 7.7 wt% had a dark brown, due to the large percentage of carbon source and oversupply of heat energy to the sample during the heating process. After irradiation with UV light, the samples with 0 wt% and 0.5 wt% CA didn’t show luminescence while the sample with 1.2 wt% CA gave the highest luminescence with a bright yellow color. The samples with 2.5 wt% to 7.7 wt% CA gave the lowest luminescence. The excess percentage of carbon source caused the sample to be heat up faster due to properties of carbon that make it absorb heat well [13].

To investigate the effect of CA mass variation (0-7.7 wt%) on the photoluminescence properties, the irradiation time was set constant at 2 minutes. The emission spectra of the samples with different CA masses are shown in Figure 5., where all samples exhibit an excitation peak at 365 nm. Figure 5 shows that the addition of carbon source mass significantly affected to intensity of the luminescence. The maximum intensity of the bright yellow was obtained in the sample with a CA mass of 1.2 wt%, with a peak wavelength of the emission spectra around 526 nm. It was verified that addition of 1.2 wt% CA mass enhances the emission efficiency of CNDs. On the other hand, the samples with CA
**Figure 4.** The produced CNDs with mass variation CA (0.5-7.7 wt%) before (samples a-e) and after (samples f-j) the ultraviolet light excitement.

**Figure 5.** PL spectra CNDs with variation CA mass (0-7.7 wt%) with heating time for 120 s.

mass 0 wt% and 0.5 wt%, didn’t give an emission spectrum due to insufficient energy to cause a reaction between C and N. Thus, the sample did not produce carbon nanodots. The sample with 7.7 wt% CA mass did produce CNDs but an excess amount of carbon caused the sample to resemble charcoal. The intensity of luminescence was reduced due to the emission color of the CNDs having
been absorbed by the carbon [3]. Furthermore, considering the increase of CA mass can change the electrical conductivity of the samples. It is important factor in microwave heating that provide requirements for effective energy heating [14, 15].

4. Conclusions
CNDs were synthesized successfully by a microwave-assisted method. A Microwave oven was equipped with an infrared thermometer and was thus able to identify the parameters of temperature and heat energy supply, so the sample’s temperature could be measured during the heating process in the microwave. Further, the amount of energy needed in the CNDs synthesis can be estimated. The amount of carbon sources affects the luminescence intensity of the CNDs. The optimum stable luminescence was produced from the sample with 1.2 wt% CA mass, which obtained a strong yellow emission with an emission peak at 526 nm.

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