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Synthesis and Material Characterizations of S-doped Carbon Nanodots from Blackstrap Molasses

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ABSTRACT

Carbon Nanodots (CNDs) are semiconductor materials with a size below 10 nm. Carbon nanodots can be applied to several areas, such as biosensors, bioimaging, optoelectronics, and photocatalysis. Current research has shown that additional dopants to CNDs such as nitrogen (N) and sulfur (S), indicate a significant increase in electronic properties and fluorescence particularly for photocatalytic applications. Blackstrap molasse is cheap and easy to obtain due to it is a side result of sugarcane production. Hence, it has potential as carbon sources for carbon nanodots synthesis and production. The synthesis of S-doped Carbon Nanodots (S-doped CNDs) based on blackstrap molasses, H_2O_2, and garlic powder has been conducted by Microwave-Assisted Extraction (MAE). Characterization by FTIR indicates several functional groups mainly OH, C=O, C-H, and C-O-C with respective wavenumber of 3254,55 cm^{-1}, 1633,56 cm^{-1}, 1323,75 cm^{-1}, and 1053,78 cm^{-1}. The presence of stretching vibration at 1268,13 $cm\text{-}^1$ as a new functional group of C-S, indicates the success of additional sulfur (S) dopant within carbon nanodots (CNDs). The fluorescence effect has been observed for carbon dots solution transforming light brown into blue color under UV light of 365 nm. These results have shown the effectiveness of the synthesis process of carbon nanodots (CNDs) from blackstrap molasses doped by sulfur from garlic using the MAE method.

Keywords: *Molasses, Garlic, Microwave-Assisted Extraction, Carbon Nanodots, S-Doped Carbon Nanodots.*

1. INTRODUCTION

Carbon nanodots (CNDs) are carbon nanomaterials with a diameter of under 10 nm. On the surface of the CNDs there are functional groups such as hydroxyl, ether, carbonyl, and carboxylic acids [1]. CNDs have high photostability, good biocompatibility, low toxicity, are easy to manufacture, and are also environmentally friendly [2]. Because of these features, CNDs have advantages over quantum dots (QDs) such as graphene quantum dots (GQDs), metal oxides (ZnO, TiO2), and inorganic QDs (ZnO-PbS, CdSe, ZnS) [3]. CNDs have the potential to be functional in several fields such as photocatalyst [4], chemo- and bio-sensing, cellular imaging, and bio labeling [5].

Since its discovery in 2004, research on CNDs has continued to develop from numerous carbon sources. Typically, there are two methods to generate carbon dots, namely through top-down and bottom-up [6]. The top-down involves a higher dimensional carbon source material (CNDs considered 0-dimensional) being broken down into a nanometer-sized material. While the bottom-up method makes use of a carbon source that forms nanometer-sized particles.

Photoluminescence has been associated with functional groups, CND conjugated π state, and surface electronic state. These characteristics can be adjusted by modifying the composition and structure of the CNDs, as well as doping with other non-metallic elements [7,8].

The application of CDs in catalysis is still in its early stages, and much work remains to be done. Although several studies have reported the potential of CNDs as photocatalysts in water purification [9]. On the other hand, the synthesis of nanomaterials always requires high energy and the use of harmful chemicals. Therefore, it is necessary to use environmentally benign raw materials and use low energy. Carbon dots from molasses have the potential to be applied as photocatalysts, apart from being environmentally friendly, molasses is also easy to attain.

The addition of heteroatoms such as nitrogen, sulfur, and phosphorus to the carbon source leads to enhance the fluorescence efficiency of CNDs through surface passivation, where the structure and optical properties of CNDs depend on the source material.

This research was conducted to determine the effect of sulfur doping on the characteristics of CNDs. In this study, molasses was used as a carbon source and garlic powder as a source of sulfur. Synthesis of CNDs was carried out using the Microwave-Assisted Extraction (MAE) method.

2. METHODOLOGY

2.1. Equipment and Materials

Glassware, microwave, and filter paper utensils for the synthesis of carbon nanodots (CNDs) from molasses. The results of the synthesis of carbon dots were characterized using the SHIMADZU UV-Vis spectrophotometer, BRUKER Fourier Transform Infrared (FTIR) spectrophotometer, and HITACHI-9500-High Resolution Transmission Electron Microscope (HRTEM).

The materials used in this experiment included molasses, garlic powder, demineralized water, and 30% H_2O_2.

2.2. Experimental Procedures

The synthesis method of S-doped carbon nanodots was modified from the experimental method conducted by Rahmayanti et al [5]. 50 grams of molasses, 4 grams of garlic powder (as a sulfur dopant), and 20 mL of 30% H_2O_2 were dissolved in 200 mL of demineralized water in a 600 mL beaker. Afterward, it was heated on a hotplate with a temperature of 70 °C and maintained for 15 minutes. The color of the solution changes from black to brown. The solution mixture was irradiated at a medium level for 2 minutes using a homemade microwave. The solution was then filtered with filter paper to separate it from the aggregate

For comparison, the non-doped carbon nanodots were also synthesized with similar carbon sources and methods without additional garlic powder.

2.3. Characterization

Fluorescence Analysis. The fluorescence properties of Sulfur-doped carbon nanodots were analyzed visually under UV light with a wavelength of 365 nm. The sample solution is placed in a quartz cuvette and then exposed to a UV lamp to see the color glow it produces. The fluorescence emissions resulting from biomass are usually blue or green.

UV Absorption Analysis. The spectra of S-doped carbon nanodots were observed in the UV region (200-400 nm) using a SHIMADZU UV-Vis spectrophotometer.

The sample solution was diluted up to 20 times with demineralized water. The presence of an absorbance peak indicates the presence of carbon dots.

Functional Group Analysis. Fourier Transform Infrared (FTIR) spectrophotometer was used to identify functional groups on sulfur-doped carbon nanodots. Each 1 mL sample of S-doped and non-doped carbon nanodots was observed by FTIR.

Particle Size Analysis with HRTEM. It is used to determine the particle size distribution and morphology of both S-doped and non-doped carbon nanodots. The examination was conducted at the Nanoscience and Nanotechnology Research Center Bandung Institute of Technology. The particle size of the S-doped carbon nanodots must be below or equal to 10 nm and the Image J software was used to define the particle size distribution.

3. RESULT AND DISCUSSION

3.1. Synthesize of S-doped Carbon Nanodots

S-doped carbon nanodots were synthesized from molasses by adding 30% H_2O_2 as a bleaching agent and followed by an irradiation process using the microwave-assisted extraction method. Powdered garlic is used as an organic sulfur dopant to produce sulfur-doped carbon nanodots. The color of the resulting mixture of molasses is a brown suspension. The synthesis process was followed by microwave irradiation of the suspension solution at a medium level for 2 minutes. The suspension solution was filtered with Whatman 42 filter paper to remove aggregates. After being filtered, the suspension solution is yellowish-brown.

3.2. Characteristics of S-doped Carbon Nanodots

The sulfur-doped and non-doped carbon nanodots suspensions were diluted 1: 5 with distilled water to avoid agglomeration and aggregate formation prior to measurements. Both suspension solutions display a blue fluorescence effect under 365 nm UV light irradiation indicating the presence of carbon nanodots, as shown in Figure 1.

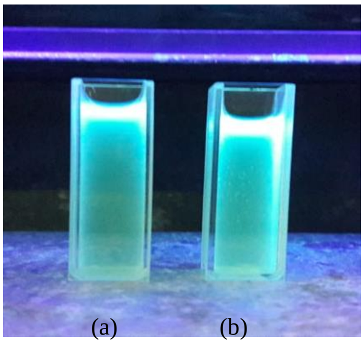

Figure 1. Fluorescence of S-doped CNDs (a) and Non-doped CNDs (b) under 365 nm UV light irradiation

The blue fluorescence emission produced by both suspension solution of carbon nanodots occurs due to an imbalance of electrons in 365 nm UV rays (Figure 1). These electrons are excited from the valence band (VB) to the conduction band (CB). The imbalance causes the electrons to return to the valence band and emit a blue color. Furthermore, the blue fluorescence produced by CNDs can also be derived from the recombination of excited electron radiation from the n - π * transition of the carbonyl (–C = O) functional group [3]. The absorbance properties of S-doped CNDs were observed using a UV-Vis spectrophotometer. Figure 2 showed maximum absorption at a wavelength of 272.5 nm. The addition of sulfur from powdered garlic resulted in a shift in the absorbance spectrum as far as 9.5 nm, whereas in the absence of dopant sulfur the absorbance spectrum showed a peak at a wavelength of 263 nm. This result however was a reverse trend from previous research findings in our group for N-doped carbon nanodots derived from blackstrap molasses. The outcome was observed when urea was used as dopant source in the N-doped CNDs synthesis. The absorbance spectrum for N-doped CNDs exhibits a peak at 220 nm. The appearance of the spectral peaks at this wavelength is due to the π-π * transition of the –C = O bond.

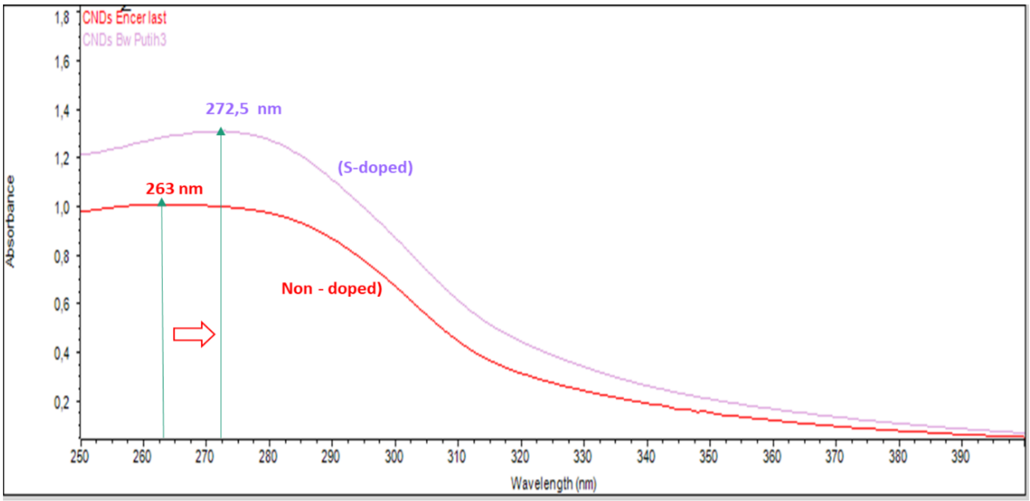

Figure 2. The Spectrum of S-doped CNDs and Non-doped CNDs in UV Waves

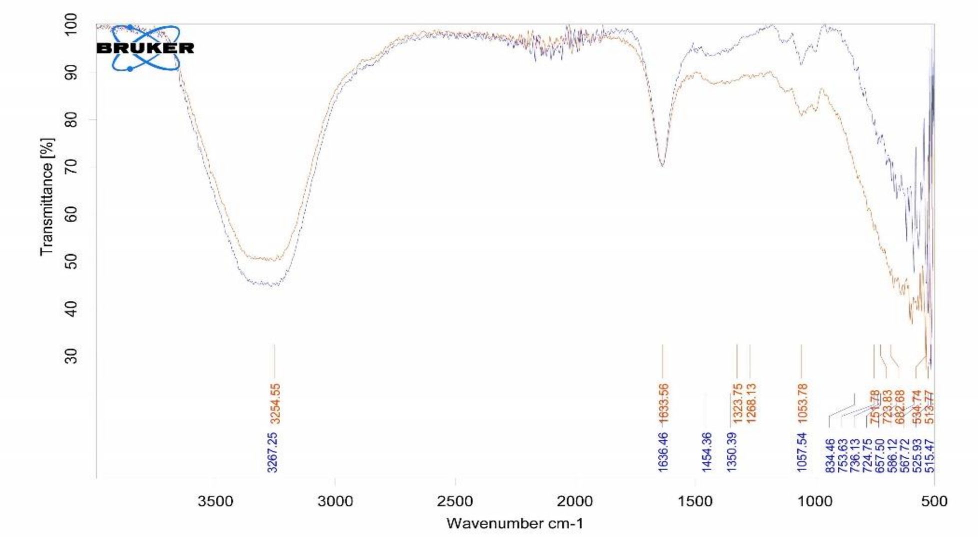

Figure 3. S-doped CNDs Infrared Spectrum (red) and Non-doped CNDs (blue)

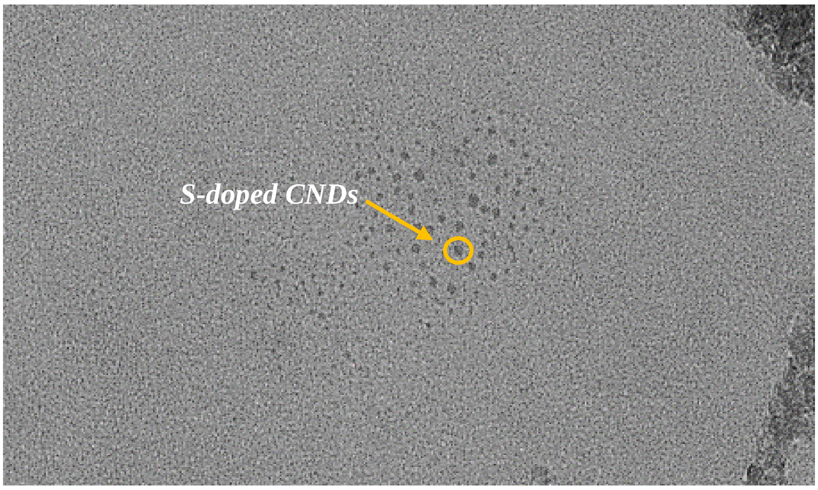

Figure 4. Morphology of S-doped CNDs

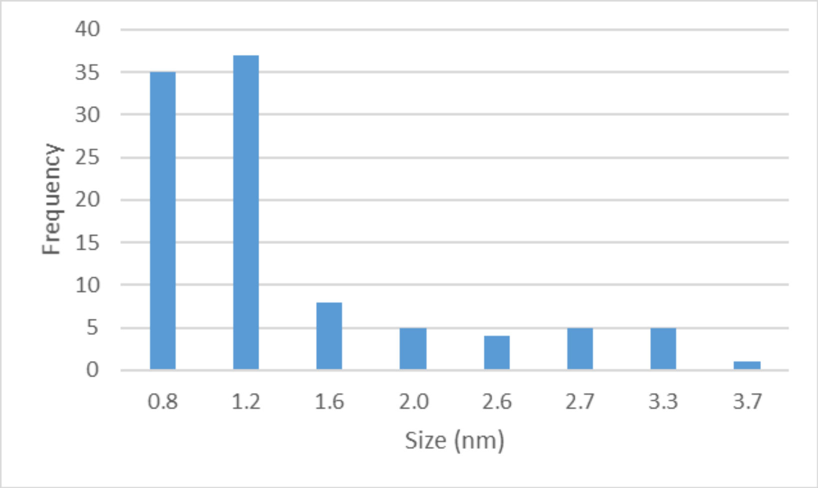

Figure 5. The particle size distribution of S-doped CNDs

Figure 3 exhibits infrared spectra of S-doped s and non-doped CNDs showing the presence of a main functional group of OH with a wavenumber of 3254.55 cm-1. Another functional group, namely C = O stretching vibration at 1633.56 cm-1 and a tiny band at wave number 1323.75 cm-1 is considered as CO group, while the C-O-C functional group appears at wave number 1053.78 cm-1. The existence of the tensile vibration that appears at the wave number 1268.13 cm-1 is a new functional group, namely C-S which indicates the success of the process of adding sulfur (S) as a dopant to S-doped CNDs.

HRTEM was used to determine the morphology of S-doped CNDs. The HRTEM results shown in Figure 4 illustrate that S-doped CNDs has a round shape and non-uniform sizes ranging from 0.8 to 3.7 nm.

The size of S-doped CNDs was calculated using Image J software and the distribution was made of frequency distribution graphs using Microsoft Excel as many as 100 data. Based on the distribution chart shown in Figure 5, it can be seen that the size of 1.2 nm is the highest frequency. The result indicates attainment in the synthesis of S-doped CNDs under 10 nm. The particle size of S-doped CNDs is related to the luminescent color produced which shifts towards the short-wavelength due to the quantum confinement effect.

4. CONCLUSION

S-doped CNDs have a blue fluorescence under 365 nm UV light with a particle size of 1.2 nm. The peak of the absorbance spectrum for S-doped CNDs appears at a wavelength of 272.5 nm and has OH, C = O, C-O, C-O-C functional groups, and C-S functional groups that show the successful synthesis of S-doped CNDs through the MAE method.

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