

SYNTHESIS OF FLUORESCENCE CARBON NANOPARTICLES FROM ASCORBIC ACID

Sri Sugiarti* and Noviyana Darmawan

Department of Chemistry, Bogor Agricultural University, Jl. Agatis, Kampus IPB Darmaga, Bogor 16680, Indonesia

Received January 15, 2015; Accepted April 16, 2015

ABSTRACT

Carbon nanoparticles (C-dot) are materials that belong to a class of 0-dimensional nanoparticles with a photoluminescence property. C-dot can be synthesized from a variety of organic acids through bottom-up synthetic methods or from other source of inorganic carbons through top-down synthetic methods. Herein, we report a simple and fast synthesis method for the formation of C-dot from ascorbic acid using microwave heating technique. The success of this synthesis was shown by visual analysis, UV-Vis spectroscopy, fluorescence spectroscopy, and transmission electron microscopy (TEM). Visual analysis showed an increased in fluorescence intensity with the addition of urea as a passivation agent. The maximum fluorescence emission of the C-dot was a blue green color at wavelength 500 nm, after the C-dot was excited at a wavelength of 400 nm. The TEM analysis showed that the synthesized C-dot had an average size of 18 nm. We also conducted a preliminary study on the synthesized C-dot as a heavy ion metal sensor and found selective identification of Cr metal.

Keywords: carbon nanoparticles; ascorbic acid; urea; microwave; metal ion sensor

ABSTRAK

Nanopartikel karbon (C-dot) merupakan material yang termasuk ke dalam kelas nanopartikel 0 dimensi yang bersifat fotoluminesen. C-dot dapat disintesis dari berbagai sumber asam-asam organik melalui metode sintesis bottom-up, atau dari sumber karbon anorganik lainnya melalui metode top-down. Kami melaporkan metode sintesis yang cepat dan sederhana untuk sintesis C-dot dari asam askorbat menggunakan teknik pemanasan microwave. Keberhasilan sintesis C-dot ditunjukkan dari analisis visual, spektroskopi UV-Vis, spektroskopi fluoresen, dan TEM. Analisis visual menunjukkan peningkatan intensitas fluoresen dengan penambahan agen pasifasi urea. Emisi maksimum fluoresen C-dot yang diperoleh berada pada panjang gelombang sinar tampak yaitu 500 nm dan berwarna hijau, setelah dieksitasi pada panjang gelombang 400 nm. Analisis TEM menunjukkan bahwa C-dot yang diperoleh memiliki ukuran rata-rata 18 nm. Kami juga melaporkan aplikasi pendahuluan dari C-dot yang dihasilkan sebagai sensor ion logam, yang menunjukkan selektivitas terhadap ion logam Cr.

Kata Kunci: nanopartikel karbon; asam askorbat; urea; microwave; sensor ion logam

INTRODUCTION

Carbon nanodots (C-dots) are materials that belong to a class of 0-dimensional carbon nanoparticles [1]. These materials are analogous to quantum dots and have structural similarity with graphite oxide particles [2]. C-dots have similar characteristics with heavy metal based quantum dots but have a number of advantages such as good solubility in water, cheap starting materials, do not contain heavy metals, efficient synthetic process, having strong photoluminescence properties, low toxicity, and good photostability [3]. These materials are widely used as photocatalysts, sensors, lasers, LED, and tools for converting or storing energy [2,4]. C-dots can be synthesized from any starting materials that contain carbon atoms, and different sources of starting material will give different fluorescence. C-dots have been synthesized from citric

acid [2], candle soot [5], soy milk [4], egg white and egg yolk [6], gum arabic [7], orange peel [8], and various amino acids [9]. Hsu et al. [10] observed that functional groups of carboxylic acid and hydroxylate on the starting material of organic compounds are very important in the synthesized of C-dot. There are two methods to synthesizing C-dots, the bottom-up and the top-down methods. The bottom-up method, a more simple synthetic process, includes synthesis using electrochemical, microwave/ultrasonic, combustion oxidation, hydrothermal, or acidic oxidation techniques. In the bottom-up method, also called chemical method, organic acids are widely used as starting material. Yang et al. [3] synthesized C-dot from citric acid using microwave method, and they also reported that when using the microwave method only simple organic compounds with molecular weight less than 800 Da can successfully produce C-dot. We chose to focus on

* Corresponding author. Tel/Fax : +62-251-8624567
Email address : sri.sw07@gmail.com

ascorbic acid because it is abundant and is a simple organic acid, similar to citric acid. Baker et al. [11] reviewed C-dot synthesis and noted that there is still no standard for C-dot as they are synthesized from many sources of carbon using different passivation agents. However, the presence of fluorescent emission from a carbonized sample is indicative of the presence of C-dot, as bulky carbon allotropes do not emit fluorescence. Many researchers have suggested that C-dot is a nanoparticle consisting of graphite and graphite oxide [11].

The fluorescence mechanism of C-dots is poorly understood, however, the consensus is that they involve an energy trapping species such as occurs in quantum dots, therefore the addition of a surface passivation agent, which should be a nitrogen containing organic molecule, can enhance emission intensity of the particle [11]. Here, we used various concentrations of urea as the passivation agent. Finally, a preliminary study was conducted on the synthesized C-dots to test their ability as a sensor for identification of metal ions.

EXPERIMENTAL SECTION

Materials

All chemicals were purchased and used without further purification. Chemicals used in this study were ascorbic acid (Merck), urea (Merck), and deionized water.

Instrumentation

Instrumentation used in the synthesis of C-dots was common laboratory glassware, analytical balance, a Sharp R-222Y 700 W microwave oven, laboratory oven, and PLC series centrifuge. Identity and purity of the products were examined by UV-Vis spectrophotometer 1700 Shimadzu, a 366 nm UV light source, and an Ocean Optic USB4000 spectrophotometer. The morphology of the products was examined by transmission electron microscope (TEM) JEM-1400 JEOL instrument.

Procedure

Synthesis of C-dot

A solution was made by diluting 1 g of ascorbic acid and 1 g of urea in 10 mL of deionized water, which was then carbonized by heating in a microwave oven for 4 min [2]. During heating, the color of solution changed from colorless to brown, and eventually a brownish black solid phase precipitated from the solution. Then, the solution containing C-dot precipitate was heated in an oven for 1 h at 60 °C. The C-dot precipitate was purified

by centrifuging the solution at 3000 rpm for 20 min, which then separated from the liquid phase and underwent a solidification process on a hot plate. To observe the effect of urea concentration on the fluorescence activity of the C-dots, various concentrations of urea was added to the starting material solution. The urea concentrations used were 0, 10, 25, 50, and 75%. All C-dots from the varying urea concentrations were characterized and analyzed using UV-Vis and fluorescence spectrophotometers, and TEM.

Application of C-dots as metal ion sensor

As much as 0.025 g of C-dots precipitate was added to a 25 mL volumetric flask, and then diluted with deionized water up to the marking volume. 1 mL each of this solution was added to 6 small vials. Then, 1 mL each of 1000 ppm of Fe^{2+} , Mn^{2+} , Cr^{6+} , Pb^{2+} , and Hg^{2+} solutions were added to separate vials containing the C-dot. Intensity of luminescence of each vial was then observed under the 366 nm UV light source.

RESULT AND DISCUSSION

Synthesis of C-dots

The bottom-up method of C-dot synthesis has been reported to include electrochemical, microwave/ultrasonic, combustion oxidation, hydrothermal, or acidic oxidation techniques. The downside of most of these techniques is that they required harsh conditions including high pressure, temperature, and acidity [11]. The microwave technique is an alternative method of C-dot synthesis under mild conditions. However, in this method, only a limited variety of precursors can be used to synthesize C-dots, with citric acid being the most commonly studied precursor. The physical and chemical similarities between citric acid and ascorbic acid led us to choose ascorbic acid as a precursor for the synthesis of C-dot. We successfully adapted the microwave oven method used by Qu et al. for citric acid, to synthesize C-dot from ascorbic acid.

The C-dots appeared as a brownish black precipitate, as seen in Fig. 1a. Percent yield of C-dot from ascorbic acid was 60%, this is similar to the yield from citric acid reported by Qu et al. [2]. The synthesized C-dots were highly soluble in the water (Fig. 1b), probably due to the presence of organic functional groups -OH and C=O on the surface of the C-dots as shown by their stretching band in the FTIR spectrum (Fig. 2). When the C-dot solution was irradiated with UV light (365 nm), it emitted a blue green fluorescent emission which indicated the success of this synthesis (Fig. 1c). Addition of urea in

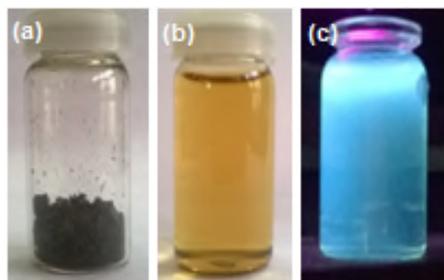


Fig 1. C-dot synthesized from ascorbic acid (a); C-dot aqueous solution (b); blue luminescent emission of C-dot (c)

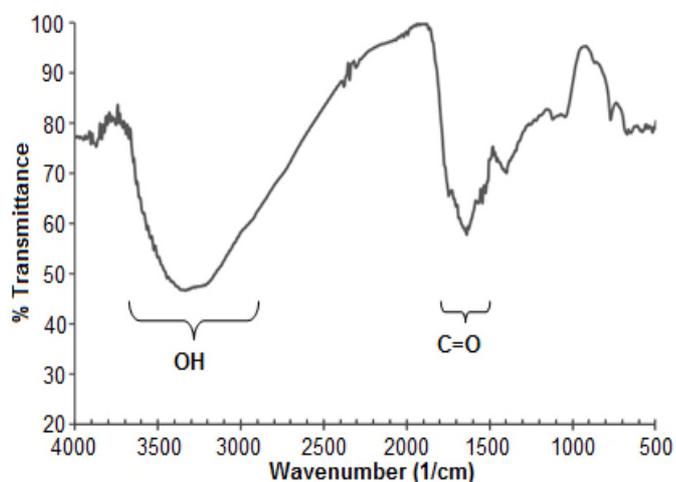


Fig 2. FTIR spectrum of C-dot synthesized from ascorbic acid

the synthesis of C-dot resulted in higher emission intensity. The highest emission intensity was shown by C-dot synthesized by adding 75% of urea to the precursor solution (Fig. 3). However, microwave heating the urea solution without ascorbic did not result in the formation of C-dot thus it can be concluded that the main precursor in this synthesis is ascorbic acid.

Spectroscopic Characterization of C-dots

UV-Vis spectroscopy analysis was done on a 100 ppm C-dot solution. The absorption spectrum of the synthesized C-dot was very different from the absorption spectrum of ascorbic acid solution (Fig. 4). The greatest difference was the increased absorption in the 300–400 nm region of C-dot spectrum which may indicate of the presence of conjugation system on the graphite oxide structure [2,4]. This result is in agreement with a previous report on C-dot synthesized from orange peel [8]. We found that the absorption peak for the C-dots and its precursor, ascorbic acid, are similar (265 nm) which indicates that there are still organic functional groups on the surface of the C-dots in agreement with

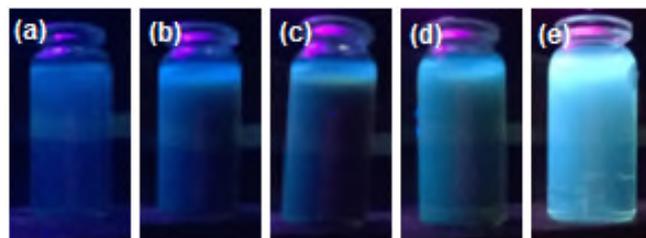


Fig 3. Increasing intensity of luminescent emission from C-dots with the lowest concentration of urea, 0%, to the one with highest concentration of urea, 75%. (a) 0%, (b) 10%, (c) 25%, (d) 50%, (e) 75% urea

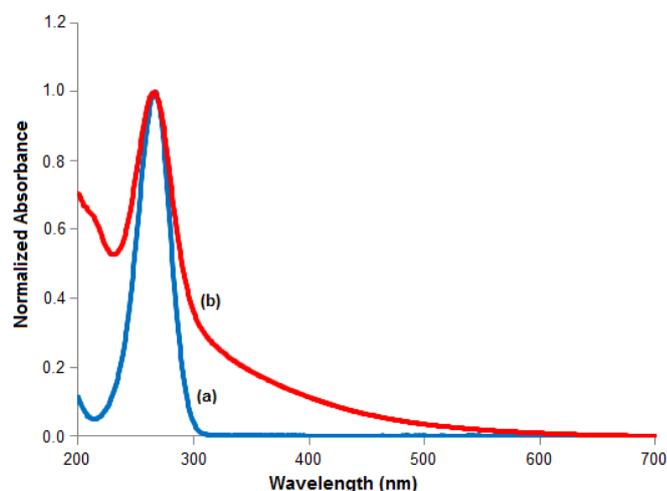


Fig 4. UV-Vis spectra of (a) ascorbic acid, and (b) synthesized C-dot

the FTIR spectrum mentioned earlier. Fig. 5 shows that the higher the urea concentration in the reaction mixture, the lower its absorption intensity. This is because with the higher the concentration of urea there is a lower concentration of C-dots, for example a sample with 75% urea, only contains 25% C-dots in the mixture and this will reduce the intensity of C-dots absorption by 75%. However, the C-dots with 75% urea showed higher luminescence intensity as noted earlier.

The maximum fluorescent emission of the C-dot was a blue green color at wavelength 500 nm, after the C-dot was excited at a wavelength of 400 nm (Fig. 6). The recorded emission spectrum was wide and structureless, which is similar to those obtained by Qu et al., and is a general characteristic of fluorescent emissions [2]. The C-dots synthesized with 75% urea had a fluorescence efficiency of 0.1, calculated using the relative method, where this value is higher compared to the one calculated for the C-dot synthesized without the addition of urea. This indicates that the passivation agent increased the emission intensity

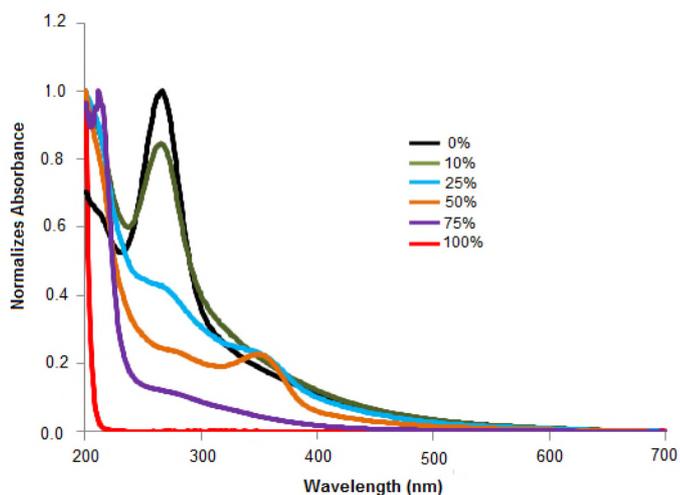


Fig 5. Effect of urea concentration on the normalized absorbance of C-dots, urea concentrations are given in color code

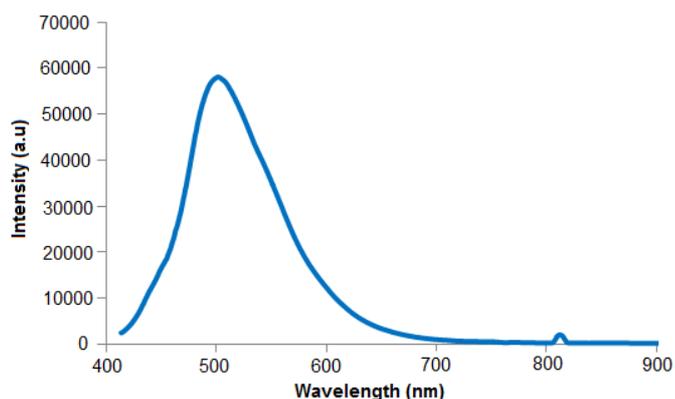


Fig 6. Fluorescence emission spectrum of C-dots synthesized with the addition of 75% urea

Characterization of C-dots Using TEM

The analysis was only done for C-dots with the brightest luminescence, the one with 75% urea. Fig. 7 shows that although some of the synthesized C-dots were round shaped, most were irregular in shape. The average size of the synthesized C-dots was 18 nm. This is in contrast with the homogeneous 1 to 5 nm round shaped C-dots synthesized from citric acid by Qu et al. [2]. This difference may be because the centrifuge technique we used in this synthesis is not very efficient to separate the particles. The use of other separating technique such as electrophoresis may yield smaller and more homogeneous C-dots. TEM analysis showed that the synthesized C-dot is amorphous, like graphite oxide. This is proved by the absence of diffraction pattern, and is similar to the the results in previous reports [2].

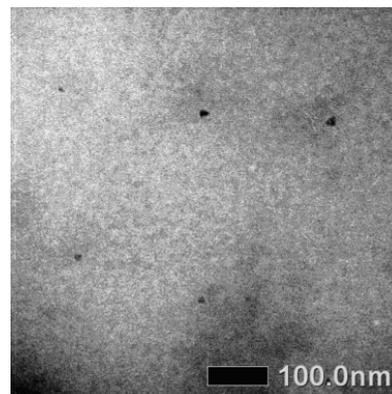


Fig 7. Representative TEM image of C-dots

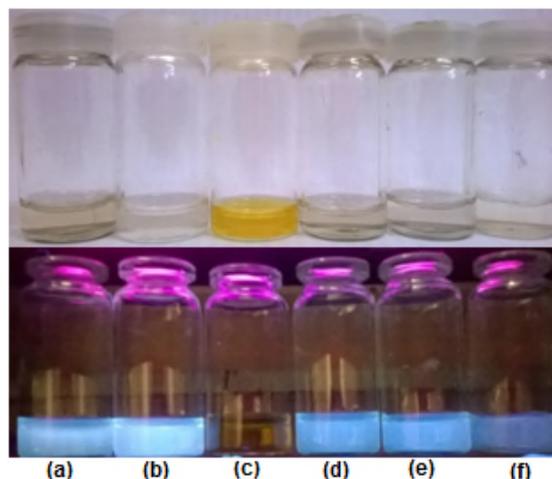


Fig 8. Selective identification of Cr^{6+} ion. The order of metal ions solutions used in the study is (a) C-dot, (b) Mn, (c) Cr, (d) Fe, (e) Pb, (f) Hg. Solutions on top were not irradiated with UV light.

Preliminary Studies on the Application of C-dots as Metal Ions Sensor

The ability of C-dots to interact with metal ions is shown by a reduction in C-dots luminescence [3]. Fig. 8 shows that the synthesized C-dots with 75% urea positively identified Cr^{6+} ion, out of the 5 metal ions used in this study. This showed that the synthesized C-dots selectively differentiated the Cr^{6+} ions from the other metal ions. The luminescence intensity of the C-dots after being added to the solution of Cr^{6+} ion was also analyzed using fluorescence spectroscopy, and showed almost no emitted fluorescence (Fig. 9). Yan et al. reported that C-dot synthesized from anhydrous citric acid with ethylene diammine as passivation agent is selective for Hg^{2+} [12].

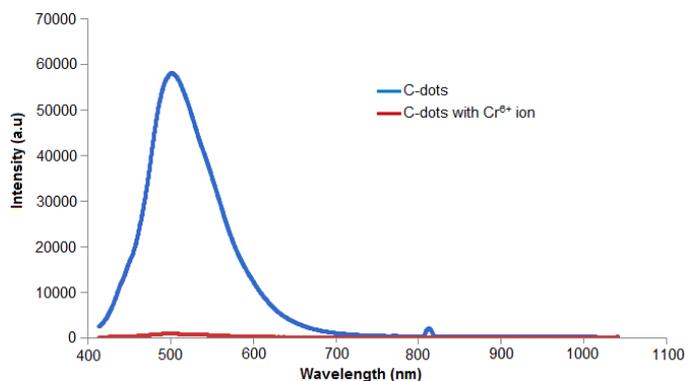


Fig 9. fluorescent emission spectrum of C-dots in the presence of Cr^{6+} ion

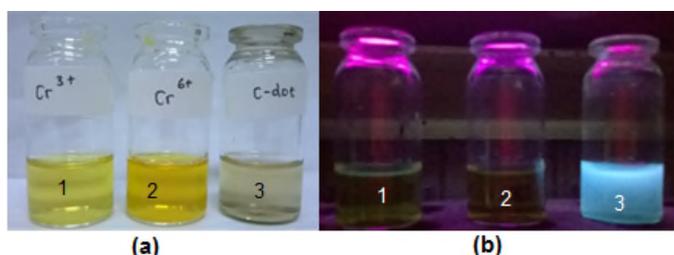


Fig 10. C-dot solution in the presence of Cr^{3+} ion (1), Cr^{6+} ion (2), and without metal ion (3); without (a) and with (b) UV light irradiation

Another test was done on Cr^{3+} ion to observe the effect of using a different source of Cr ion. Fig. 10 showed that there is no significant response between Cr^{6+} and Cr^{3+} ions. This result showed that the resulted C-dot selectively identified Cr metal, however cannot differentiate the type of Cr ions.

CONCLUSION

Blue green fluorescent emitting C-dots were synthesized quickly and easily by microwave heating ascorbic acid. Emission intensity increased with the

addition of urea as a passivation agent in the reaction process. Preliminary study showed the potential for the synthesized C-dots to serve as heavy metal sensors.

ACKNOWLEDGEMENT

The authors would like to thanks Ms. Awalia Khairunnisa for her help in the preliminary study, and Mrs. Lilis Sulistiawaty for her help in the analysis of C-dot using TEM.

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