Journal of the Korean Chemical Society
2021, *Vol. 65, No. 4*
Printed in the Republic of Korea
https://doi.org/10.5012/jkcs.2021.65.4.296

Note

Excitation Wavelength-dependent Characteristics of Fluorescent Carbon Nanodots

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(Received April 26, 2021; Accepted May 18, 2021)

Key words: Fluorescent carbon nanodots, Microwave-assisted method

Carbon nanodots have emerged as a novel class of carbon-based materials since they were discovered accidentally during the electrophoretic purification of single-walled carbon nanotubes.[1] The carbon nanodots typically have quasi-spherical shape and discrete sizes of a few tens of nanometers. In general, carbon materials are not luminescent and not very soluble in water. However, carbon nanodots can be made soluble in aqueous media since hydrophilic groups such as carboxylic acid moieties are introduced at the surface of nanodots during the process of formation. The surface carboxylic group can be subsequently modified into different functional groups for various purposes. One of the interesting features of carbon nanodots is their photoluminescent property, which is dependent on the size of nanodots and the excitation wavelength. Carbon nanodots can be processed chemically stable, and biologically compatible. Due to their unique photochemical and photophysical properties, carbon nanodots attracted a great deal of interests in the area of fluorescent nanomaterial applications such as biological imaging, optical sensors, and light-emitting devices.[2–4] To date, a variety of synthetic methods including chemical ablation, laser ablation, hydrothermal treatment, microwave irradiation etc., have been introduced to produce fluorescent carbon nanodots.[3,4,6] Some progresses have been made in the synthesis of carbon nanodots, but there are still many problems and issues to be addressed about controlling the particle size, uniformity, nanostructure, and surface properties in order to find useful applications in utilizing the fluorescent carbon nanomaterials. Photoluminescence properties have been studied for a variety of carbon nanodots. For last decades, a wide range of fluorescence carbon nanodots with varying particle sizes and different luminescent colors have been prepared and their photophysical and photochemical characteristics were investigated.[7,8] Most of carbon nanodots studied show the excitation wavelength dependent fluorescence. Zhao *et al*., attributed this finding to the size difference of nanodots, [9] and Sun *et al.*, suggested the distribution of emissive trap sites as well as the difference in size are responsible for the wavelength dependent emission.[10] Fluorescence quantum yield of carbon nanodots is in most cases very low, but recent studies reported that surface passivation could increase the fluorescence quantum yield.[11,12] Photoluminescence decay studies show the multi-exponential nature of fluorescence lifetime, which indicates the presence of different emissive sites.[7,10] Several explanations such as quantum size effect, defects and surface states, surface passivation, π-conjugation of fluorophore, electron-hole pair recombination in carbon clusters are given to the origin of the fluorescence. Even with all those ongoing studies for newly prepared fluorescent carbon nanodots, their photoluminescence origins are still not very clear and the mechanism for fluorescence is not well understood. It is considered that the fluorescence characteristics of carbon nanodots are very much affected by specific methods of preparation and conditions related to an individual synthetic method.

Carbon nanodots can be synthesized by either top-down or bottom-up approaches. In top-down methods, carbon nanodots are formed by breaking down larger carbon materials such as graphite or graphene, whereas in bottom-up methods carbon nanodots can be formed by decomposition and carbonization of small or large organic precursor molecules.[13] In this work we have applied a microwave-assisted method, and an electrochemical method for the synthesis of carbon nanodots. The size and cluster structure of carbon nanodots are studied using a transmission electron microscope. The spectroscopic characteristics of the prepared carbon nanodots are investigated by electronic absorption and emission spectroscopy. In addition to the carbon nanodots, boron-doped carbon nano-

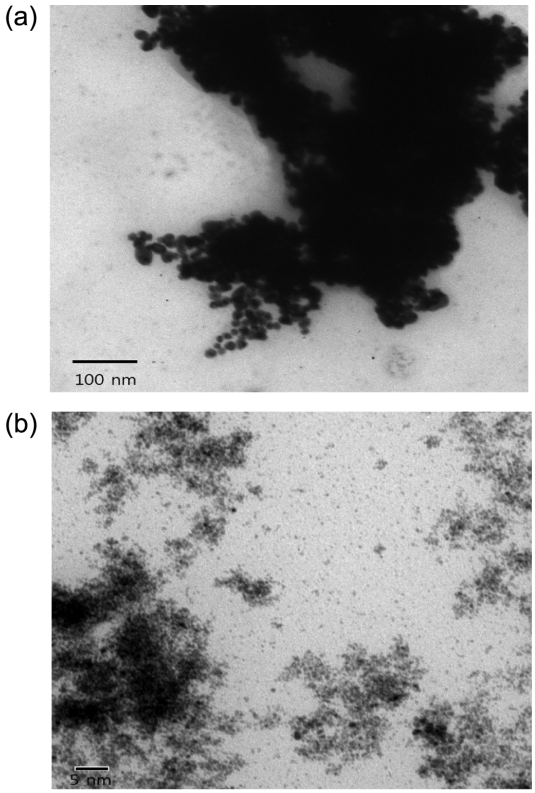

***Figure* 1.** TEM images for (a) carbon nanodots synthesized by a microwave-assisted method shown with 100 nm scale bar (b) carbon nanodots synthesized by an electrochemical method shown with 5 nm scale bar. The images were taken by the field emission transmission electron microscope (Hitachi/HF-3300).

dots[14] were also prepared and their fluorescence properties were studied and compared with the undoped ones.

Size Distribution of Carbon Nanodots

The formation of carbon nanodots is identified by the field emission transmission electron microscope (Hitachi/HF-3300) and their size was estimated. *Fig.* 1 shows the TEM images of carbon nanodots prepared by a microwave-assisted method and an electrochemical method. The average particle size for the carbon nanodot synthesized by a microwave-assisted method is estimated to be about 15-20 nm in diameter, meanwhile the carbon nanodots prepared by an electrochemical method are much smaller than the former ones and estimated to be sub-nanometer size.

Absorption and Photoluminescence Properties

The UV/Vis absorption spectra of carbon nanodots prepared using two different synthetic methods are shown in *Fig.* 2.

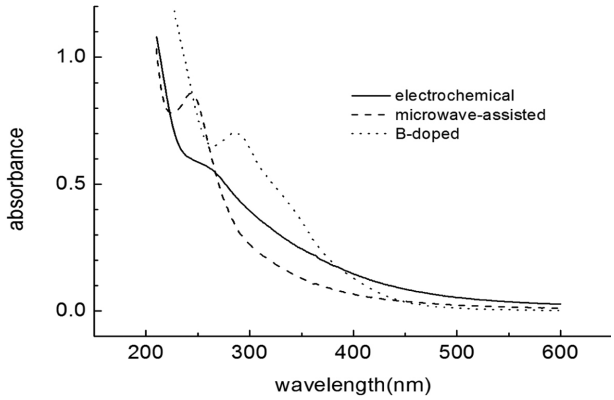

***Figure* 2.** Electronic absorption spectra of carbon nanodots synthesized by (a) a microwave-assisted method (----), (b) an electrochemical method (—), and (c) B-doped carbon nanodots (····).

They indicate similar absorption features even though their spectral shapes might be slightly varied depending on the preparation methods. It is typical that strong absorption peak is observed in 230-300 nm region with the absorption edge extending all the way down to ~550 nm. The absorption peak observed in ultraviolet region is attributed to π-π* transitions of C=C bond, and this peak is more prominent for the carbon nanodots prepared by a microwave method and weakly observed for carbon dots prepared by an electrochemical method. The UV/Vis absorption spectrum for B-doped carbon nanodots are also included for comparison. The π-π* transition peak of B-doped carbon nanodots shifted to lower energy absorption compared to the undoped ones, and there is a weak unresolved shoulder band as shown in the figure.

The photoluminescence property is one of the interesting topics for the applications of carbon nanodot materials. The fluorescence spectra for the carbon nanodots prepared by a microwave-assisted method were measured at several excitation wavelengths and shown in *Fig.* 3. The fluorescence spectra have broad bandwidth with the peak wavelength centered around 439 nm. The peak of fluorescence band does not seem to change as excitation wavelength varies.

Fig. 4 shows the fluorescence spectra for the carbon nanodots prepared by an electrochemical method. As excitation energy decreases, i.e., the excitation wavelength shifts to red, a red shift in the emission spectra is observed. In contrast with the observation made for microwave-assisted carbon nanodots where the fluorescence peak position does not change, now it shifts in relation to the excitation wavelength. This is manifested in the inset of the figure. The excitation wavelength dependence of the

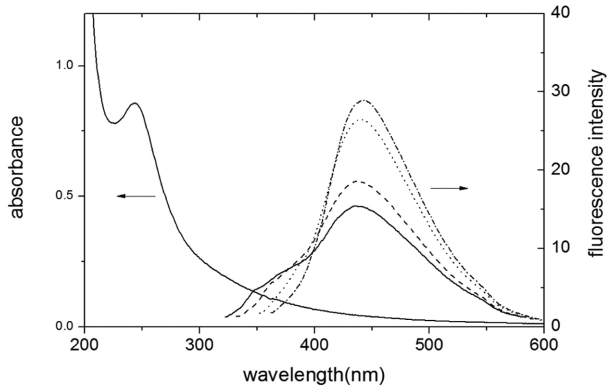

***Figure* 3.** Fluorescence spectra of carbon nanodots synthesized by a microwave-assisted method. Fluorescence was measured for different excitation wavelengths. λ_{ex} =300 nm (—), λ_{ex} =310 nm (----), λ_{ex} =320 nm (····), λ_{ex} =330 nm (-·-·-·).

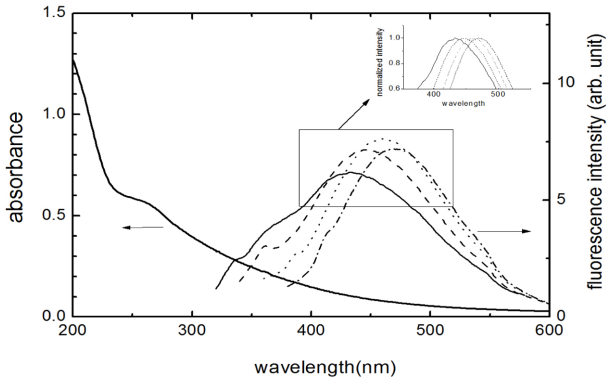

***Figure* 4.** Absorption and fluorescence spectra of carbon nanodots synthesized by an electrochemical method. Fluorescence spectra were obtained for different excitation wavelengths. λ_{ex}=300 nm (—), λ_{ex}=330 nm (----), λ_{ex}=340 nm (····), λ_{ex}=350 nm (-·-·-·). The inset shows the normalized fluorescence peaks.

emission peak may result from the size distribution of carbon nanodots or may be related to the surface chemical groups.[9,10] It was observed that the carbon nanodots produced by microwave-assisted method gives slightly larger fluorescence quantum yield than those by electrochemical method. However, the overall fluorescence efficiency is low and measured to be about ~3% at best as shown in *Table* 1.

There have been many efforts to enhance fluorescence quantum yield of carbon nanodots. The effective way of enhancing quantum yield is surface modification or passivation. In this study, Boron-doped carbon nanodots were produced and two- to three-fold increment of fluorescence quantum yield was observed. Additionally, the emission spectra of boron-doped carbon nanodots (B-CNDs) is shifted to red with peak wavelength of 454 nm, which is about 15 nm red-shifted compared to the undoped one.

***Table* 1.** Fluorescence quantum yield of carbon nanodots

Carbon nanodots	Absorbance	Fluorescence intensity (arb.)	ϕ_{fl}
Microwave assisted	0.035	1622±32	2.95×10^{-2}
Electrochemical	0.053	1350±27	1.63×10^{-2}
B-doped	0.088	10459±209	7.95×10^{-2}

Fluorescence quantum yields were determined using 9,10-diphenyl anthracene as a standard (ϕ_{fl} = 0.95 in cyclohexane) at 350 nm.

In summary, fluorescent carbon nanodots were prepared by using a microwave-assisted and an electrochemical method, and their photoluminescent properties were investigated. Carbon nanodots prepared by microwave-assisted method do not exhibit any peak shift in fluorescence spectra as the excitation wavelength changes. However, the fluorescence of carbon nanodots prepared by electrochemical method show red shift on increasing excitation wavelength. Carbon nanodots by the microwave- assisted method give higher fluorescence quantum yield, and the fluorescence appears at shorter wavelength than those produced by the electrochemical method. The size distribution and spectral properties of carbon nanodots vary depending on different preparation methods. It was noted that the fluorescence of carbon nanodots was enhanced by doping with boron and the emission wavelength of carbon nanodots can be tuned by the doping.

EXPERIMENTAL

Microwave-assisted Method

(i) Preparation of carbon nanodots: 0.5 g β-D-Glucose (Sigma Aldrich) dissolved in 10 mL of distilled water was mixed with 10 ml of polyethylene glycol 200 (Duksan Chemical Co.). The reaction mixture is irradiated with microwave for 3 minutes in 800W microwave oven (Panasonic). The colorless solution turns into light yellow and later into dark brown as the microwave heating proceeds. The obtained dark brown solution is cooled and dialyzed by 100 kDa membrane (Viskase Co.) for 24 hrs. A solution of yellow color is finally obtained after the dialysis. (ii) Preparation of B-doped carbon nanodots: 0.5 g of β-D-Glucose(Sigma Aldrich) and 5mL of polyethylene glycol 200 are dissolved in ~15 mL of distilled water. Boric acid solution of 0.05 g boric acid(Duksan Chemical Co.) in 10 ml of distilled water is prepared and then mixed with glucose/polyethylene glycol solution.[14] The reaction mixture is heated with microwave for about 6 minutes.

Electrochemical Method

Electrochemical carbonization of ethanol was carried out in basic condition. Two Pt sheets as the anode and cathode are placed in the solution mixture of ethanol, distilled water, and NaOH where NaOH/EtOH was used as an electrolyte. A constant voltage of 3.0 V is applied to the electrode for about three hours. It is reported that the electrochemical oxidation of alcohols in basic solution can produced hydroxy/alkoxy free radicals and carbonium ions.[15,16] As the carbonization proceeds with time, it was observed that the initial transparent solution mixture changes its color to yellowish, and later to dark brown. After removal of ethanol by heating, and NaOH by 100 kDa dialysis membrane, carbon nanodot solution is obtained.

Acknowledgments. This work was supported by a research grant from Daegu University.

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