

FLUORESCENT CARBON DOTS PREPARED THROUGH THERMAL PROCESSING OF SUCCINIMIDE

C. ALBU, P. HORLESCU*, C. S.STAN, M. POPA
“Gheorghe Asachi” Technical University of Iasi, Dimitrie Mangeron Blvd.,
No. 67, 700050 Iasi, Romania

In this work, we report a simple, low-cost synthesis procedure of fluorescent Carbon dots (C-Dots) through pyrolytic processing of succinimide. The resulted C-Dots presents excitaton dependent fluorescent emission located in the blue interval of the visible spectrum. The average size of the resulted C-Dots is about 2-5 nm. The structure and morphology of the synthesized carbon nanoparticles were investigated through FT-IR, P-XRD, DLS, AFM, TEM while their luminescent properties were investigated in detail by steady-state and lifetime fluorescence. The recorded absolute PL quantum yield varies between 11.23 to 23.45% according to the excitation wavelength. Their photoluminescent properties, low toxicity and convenience of fabrication are only of the few arguments for applications ranging from biolabeling to optoelectronic devices.

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1. Introduction

Carbon Dots are new members of the carbon nanomaterials class that includes fullerenes, grapheme, graphite oxide or carbon nanotubes. Generally, they contain sp^2/sp^3 hybridized carbon in a graphitic core with various functional groups such as amino, carboxyl or hydroxyl groups attached on the surface [1]. C-Dots are generally very small carbon nanoparticles > 10 nm, depending on their preparation conditions and precursors. One of the most interesting features of C-Dots is their excitation dependent photoluminescent (PL) emission. Generally, C-Dots have strong absorption in the ultraviolet region, which can also is extended to visible region, usually their emission being located in blue-green and even red regions of the visible spectrum [2, 3].

Luminescence properties of Carbon Dots seems to be rather a result of the radiative transitions occurring within or between the functional groups located on the C-Dots surface and seem to be less dependent on their size. The PL mechanism relying on functional groups attached on the surface of the C-dots may provide an additionally insight on observed excitation wavelength dependence of the emission peaks. Recent studies emphasize the role of functional groups such as carbonyl, carboxyl and nitrogen containing groups in PL properties of C-dots and the possibility to alter the PL emission through modification of these surface localized groups. Several very recent studies attribute the origin of the C-Dots photoluminescence to certain organic fluorophores created during the thermal destruction of the primary precursor [4]. During the synthesis, carbonaceous nanostructured species are also produced but their PL emission is less intense. While the emission peak of the organic fluorophore is independent of the excitation wavelength, the C- Dots resulted from the thermal process behave in a “classic” manner with excitation dependent emission peaks. In another view, C- dots are seen as a blend of polycyclic aromatic hydrocarbons (PAH) with their PL properties resulting from the inner emissive states of each species [5]. This model, according to the authors view, could explain both the large Stokes shifts and the excitation dependent emission of the C-Dots which is a result of slightly different energy gaps of each of the PAHs.

* Corresponding author: elahorlescu@tuiasi.ro

Their PL properties, biocompatibility, stability and low toxicity make them interesting materials for numerous promising applications, in bioimaging, biomedicine [6,7,8], sensors [9], photovoltaics, special purpose printing inks [10] electronic and optoelectronic devices [11-13]. An increasing number of preparation routes were reported, generally divided into two main categories: chemical and physical methods, such as: chemical ablation, electrochemical carbonization, microwave or ultrasound assisted, arc discharge, laser ablation, plasma treatment etc. [14]. A major advantage is the multitude of precursors used in the preparation of C-Dots, the most interesting being the use of citric acid [15], coffee[16], N-hydroxysuccinimide [17], folic acid [18], glucose [19], straw [20], lime [21], *Trapa bispinosa* [22]. Guo and his coworkers synthesized a series of multicolor C-Dots by the thermolysis of epoxy group containing polystyrene microspheres. C-Dots produced under 200, 300, and 400°C could emit blue, orange, and white fluorescence with the excitation of single ultraviolet wavelength, while the fluorescent quantum yield is 47% [23]. In a recent work, Lin et collaborators presented a facile approach for preparation of photoluminescent (PL) carbon dots (CDs) using as precursor phenylenediamines (three isomers: o-phenylenediamine, m-phenylenediamine, and p-phenylenediamine). They report the preparation of multicolor photoluminescent C-Dots, having red, green, and blue; primary colors emission using the three different phenylenediamines isomers, through a facile solvothermal method [24].

In the present study, a facile synthesis route through pyrolytic processing of succinimide leading to photoluminescent C-Dots, is presented. The prepared C-Dots have all the specific features such are: excitation dependent PL emission, luminescence lifetimes in ns range and blue to green emission peaks.

2. Experimental

2.1 Materials

Succinimide (2,5-Pyrrolidinedione) (SI) (95%) was purchased from Sigma-Aldrich. Reagent grade ethanol (EtOH), acetone and high purity Milli-Q water were used for preparation and washing operations.

2.2 Preparation

The C-dots were prepared as follows: 4g of SI were added in a 50 ml three neck Schlenk flask provided with a magnetic stirrer and a temperature controlled heating mantle. The temperature is raised to the melting point of SI ($\approx 125^{\circ}\text{C}$) when the magnetic stirring is started. From this stage, the reaction proceeds under N_2 atmosphere with the temperature being gradually raised (about $10^{\circ}\text{C min}^{-1}$) to 175°C and maintained at this value for 20 minutes. During this process, the aspect of reaction mass changed from light yellow to brown and finally to dark-brown clustered solid which indicates the formation of C-dots. The pyrolytic process which undergoes in the ante-mentioned conditions is illustrated in Figure 1.

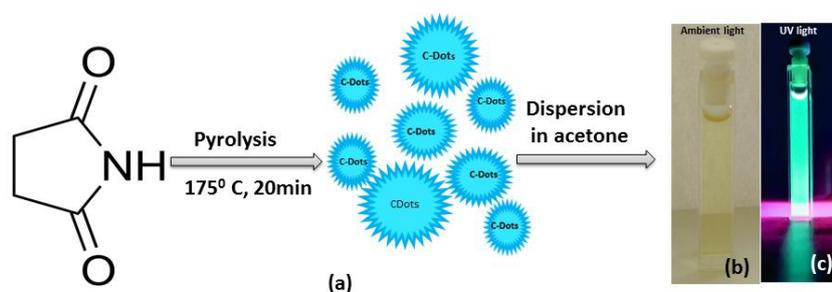


Fig. 1.(a) Schematic illustration of the C-Dots preparation path, (b) C-Dots dispersed in acetone in ambient lighting conditions, (c) under UV-A excitation

The reaction mass was allowed to cool down at room temperature and then dispersed in 45 ml of water. The mixture is centrifuged at 5000 RPM for about 20 min. The resulting deep brown tinted supernatant is collected and additionally centrifuged at 15 000 RPM for 10 min. Again, the resulting brownish tinted aqueous supernatant containing dimensionally selected C-dots is collected and further freeze dried. The dried C-dots were kept as such or re-dispersed in water, EtOH or acetone for investigation purposes.

2.3 Methods

The IR spectrum was recorded in the 4000–400 cm^{-1} range, using a Digilab FTS-2000 FT-IR spectrometer, according to KBr pellet method. The P-XRD pattern was recorded in the 10–85^o 2-theta range, on a Panalytical X'Pert Pro diffractometer provided with a Cu-K α radiation source ($\lambda = 0.154060$ nm). The dimensional investigation of the water dispersed C-Dots was performed by dynamic light scattering analysis using a Shimadzu SALD-7001 equipment. The AFM investigation was performed using an Ntegra Spectra (NT-MDT, Russia) instrument operated in tapping mode under ambient conditions. Silicon cantilever tips (NSG 10) with a resonance frequency of 140–390 kHz, a force constant of 5.5–22.5 Nm^{-1} and 10 nm tip curvature radius, were used. The sample was prepared by spin-coating the acetone dispersed C-dots on a glass slide at 1300 RPM using a Laurell WS-400-6NPP Spin Coater. TEM imaging was performed by means of Hitachi HT-7700 equipment, operated at 100 kV accelerating voltage, in high contrast mode. The C-dot samples were deposited from a highly diluted solution on 300 mesh carbon plated copper grids. Steady-state fluorescence, absolute quantum yields (PLQY) and lifetime measurements were performed on a Horiba Fluoromax 4P provided with the Quanta- ϕ integration sphere and TCSPC module.

3. Results and discussion

3.1 FT-IR investigation

The recorded spectrum of the prepared C-dots (Figure 2) is quite similar to the one recorded for the unprocessed succinimide. This situation is a result of the controlled pyrolytic processing which avoids the complete thermal destruction of the precursor. Thus, beside the formation of the graphitic core, the surface is decorated with various remnant functional groups which are involved in the radiative processes underlying the photoluminescent emission.

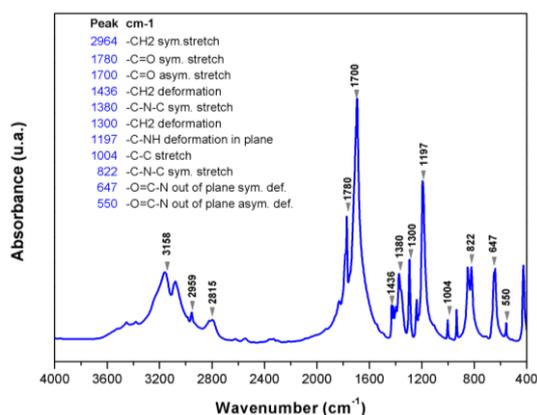


Fig. 2. FT-IR spectrum recorded for the prepared C-Dots including functional groups assignment

Although most of the peaks related to various functional groups are still present, in certain cases they are displaced, most probably, due to the structural rearrangements achieved through thermal processing. Thus, among the most notable, $-\text{C}=\text{O}$ asym. stretch is displaced from 1715 to

1700 cm^{-1} , $-\text{C}=\text{O}$ sym. stretch from 1773 to 1780 cm^{-1} , $\text{O}=\text{C}-\text{N}$ out of plane sym. deformation from 640 to 647 cm^{-1} while the $-\text{CH}_2$ sym. Stretch is displaced from 2956 to 2964 cm^{-1} .

3.2 XRD investigation

Figure 3 shows the XRD pattern recorded for the investigated C-dots. The relatively broad single peak centered at $28.26^\circ 2\theta$, is similar to other approaches reporting C-Dots preparation and investigation [25]. Compared to classic graphite peak, in case of the prepared C-Dots the broad peak is slightly shifted upward from $26.4^\circ 2\theta$ to $28.26^\circ 2\theta$ most probable due to a decrease in spacing between the carbon layers in the case of the C-dots.

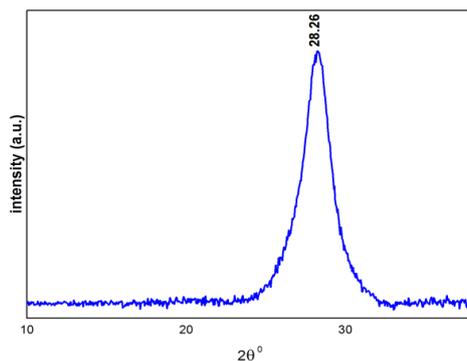


Fig 3. Recorded XRD pattern of the prepared C-Dots

3.3 Dimensional investigation

In Figure 4 is presented the size distribution recorded for a sample of C-Dots dispersed in acetone. The prepared C-Dots present an agglomeration tendency, being organized in clusters. As could be noted, the average dimensions are located in the 15-30 nm range, the results being in accordance with those recorded in case of AFM investigation.

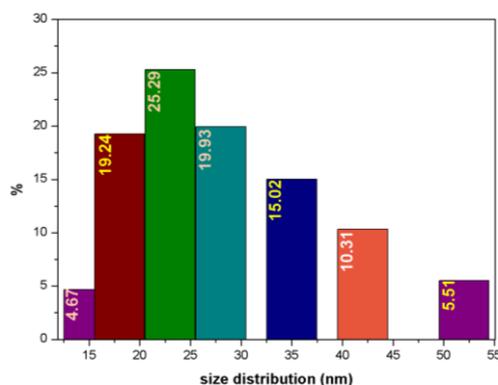


Fig. 4. Size distribution of the prepared C-Dots

3.4 AFM investigation

To avoid the agglomeration tendency, a high diluted solution of C-Dots dispersed in acetone was spin coated on a glass slide prior to investigation. The recorded AFM image (Figure 5 a,b) revealed the existence of both small particles in the range of 20–50 nm but, smaller species being discernable as well. As mentioned above, the results are in good agreement with those recorded from DLS analysis.

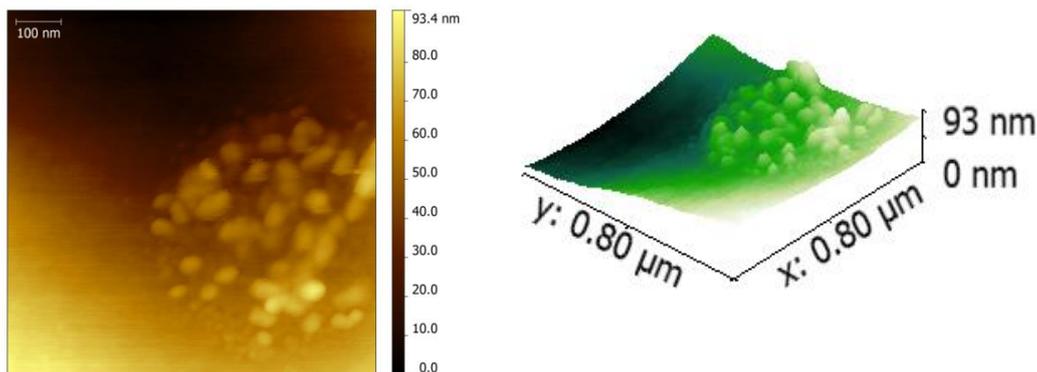


Fig. 5. (a) Recorded AFM image; (b) projected 3D image of the C-Dots

3.5 TEM investigations:

Figure 6. a, b presents the TEM micrographs recorded at two resolutions. While the Figure 6a. highlights the presence of nanostructured entities with a regular round shape, the higher resolution image revealed a nanostructure which suggests a cluster organisation, smaller entities with average dimensions in the 2-5 nm range being visible.

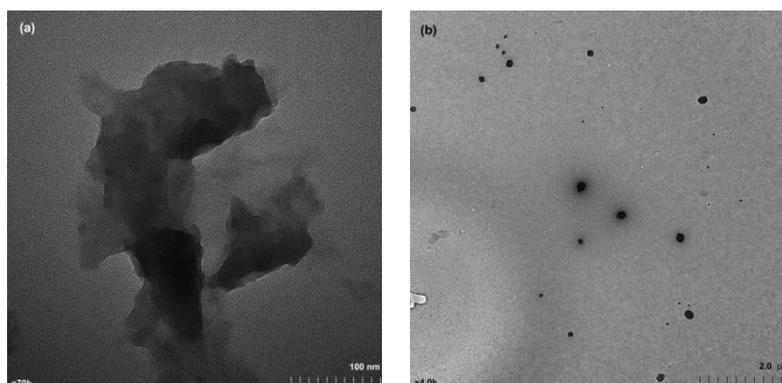


Fig. 6. TEM micrographs recorded for the investigated C-dots

3.6 Fluorescence spectroscopy

C-dots prepared through the method described above, presents all the specific characteristics which were also reported in other works, the most important being the dependence of the the emission peak on a certain specific excitation wavelength. This behavior could be easily noticed from the steady-state fluorescence spectra (Figure 7) which were recorded in the 350–450 nm (10 nm steps) excitation range. Also the spectra present same broader shape, with an average FWHM of 70-80 nm. All the recorded emission spectra were performed in the same measurement conditions in order to highlight the difference between the intensities.

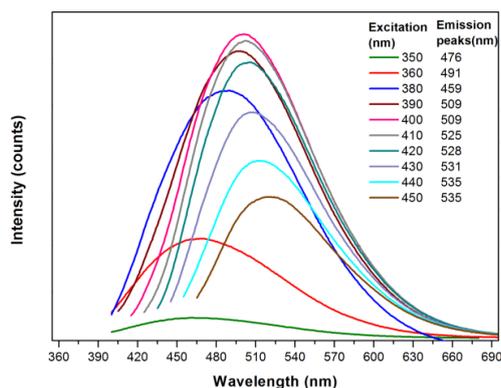


Fig. 7. PL emission spectra recorded for excitation wavelengths from 350 to 450 nm for the prepared C-dots dispersed in acetone

The most intense emission located at 509 nm was recorded with an excitation wavelength located at the upper edge of the visible spectrum (400 nm) which also corresponds to the highest recorded PLQY (Table 1). The values recorded for the absolute PLQY measurements shows values between 11.23 and 23.45% according with the excitation wavelength. In Table 1 are presented values recorded at different excitation wavelengths. The highest PLQY was achieved at 400 nm⁻¹.

Table 1 Absolute PLQY value of the C-dots dispersed in acetone

Sample/solvent	Absolute PLQY %				
	Excitation wavelength (nm)				
	350	360	380	390	400
C-dots/acetone	11.23	14.45	16.68	20.88	23.45

In Figure 8 is presented the luminescence decay recorded for the same acetone dispersed C-Dots sample. The lifetime is located in 3-5 ns range indicating short lived radiative processes involved in the PL mechanism of the C-Dots.

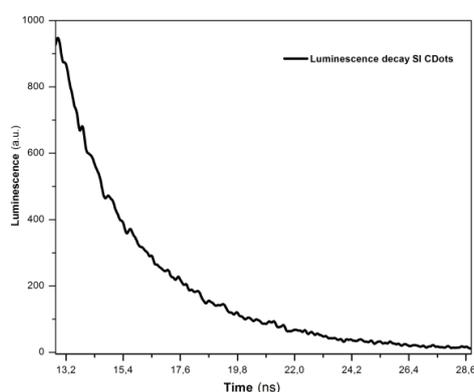


Fig. 8. Luminescence decay recorded for the investigated C-Dots dispersed in acetone

4. Conclusions

In summary, the work describe a facile synthesis route of photoluminescent Carbon Dots through a controlled pyrolytic processing of succinimide. The resulted C-Dots presents excitaton dependent fluorescent emission located in the blue range of the visible spectrum and an absolute PLQY of 23.45%. The structure and morphology of the prepared C-Dots were investigated

through FT-IR, P-XRD, DLS, AFM, TEM while their luminescent properties were investigated in detail by steady-state and lifetime fluorescence. Their photoluminescent properties, low toxicity and convenience of fabrication should recommend them for applications ranging from biolabeling to optoelectronic devices as photonic conversion mediums.

Acknowledgements

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References

- [1] Y. P. Sun, P. Wang, Z. Lu, F. Yang, M. J. Meziani, G. E. LeCroy, Y. Liu, H. Qian, *Sci. Rep.* **5**, 12354 (2015).
- [2] S. Zhu, Y. Song, X. Zhao, J. Shao, J. Zhang, B. Yang, *Nano Res.* **8**, 2 (2015).
- [3] J. Ge, Q. Jia, W. Liu, L. Guo, Q. Liu, M. Lan, H. Zhang, X. Meng, P. Wang, *Adv. Mater.* **2**, 28 (2015).
- [4] Y. Song, S. Zhu, S. Zhang, Y. Fu, L. Wang, X. Zhao, B. Yang, *J. Mater. Chem. C* **3**, (2015).
- [5] M. Fu, F. Ehrat, Y. Wang, K. Z. Milowska, C. Reckmeier, A. L. Rogach, J. K. Stolarczyk, A. S. Urban, J. Feldmann, *Nano Lett.* **15**, 9 (2015).
- [6] H. Liu, Q. Wang, G. Shen, C. Zhang, C. Li, W. Ji, C. Wang, D. Cui, *Nanoscale Res. Lett.* **9**, 397 (2014).
- [7] M. P. Sk, A. Jaiswal, A. Paul, S. S. Ghosh, A. Chattopadhyay, *Sci. Rep.* **2**, 383 (2012).
- [8] A. Talib, S. Pandey, M. Thakur, H. F., A. Talib, S. Pandey, M. Thakur, H. F., *Mat. Sci. Eng. C Mater. Biol. Appl.* **48**, 700-3 (2015).
- [9] P. Ni, H. Daia, Z. Lia, Y. Sun, J. Hua, S. Jianga, Y. Wang, Z. Li, *Talanta* **144**, (2015).
- [10] S. Qu, X. Wang, Q. Lu, X. Liu, L. Wang, *Angew Chem Int Ed Engl.* **51**, 49 (2012).
- [11] H. Li, Z. Kang, Y. Liu, S. T. Lee, *J. Mater. Chem.* **22**, 46 (2012).
- [12] X. Li, M. Rui, J. Song, Z. Shen, H. Zeng, *Adv. Funct. Mat.* **25**, 31 (2015).
- [13] N. Hui, L. Minjie, J. Bo, Z. S. Xiaolan, *Chem. J. Chinese U.* **36**, 2 (2015).
- [14] V. Georgakilas, J. A. Perman, J. Tucek, Radek Zboril, *Chem. Rev.* **115**, 11 (2015).
- [15] M. L. Bhaisare, A. Talib, M. Shahnawaz Khan, S. Pandey, H. F. Wu, *Microchim. Acta* **182**, 13 (2015)
- [16] C. Jiang, H. Wu, X. Song, X. Ma, J. Wang, M. Tan, *Talanta* **127** (2014).
- [17] C. S. Stan, C. Albu, A. Coroaba, M. Popa, D. Sutiman, *J. Mater. Chem. C* **3**, 789 (2015).
- [18] A. Mewada, S. Pandey, S. Shinde, N. Mishra, G. Oza, M. Thakur, M. Sharon, M. Sharon, *Mat. Sci. Eng C* **2**, (2014).
- [19] E. F. Simões, J. C. da Silva, J. M. Leitão, *Anal. Chim. Acta.* **852** (2014).
- [20] M. Yuan, R. Zhong, H. Gao, W. Li, X. Yun, J. Liu, X. Zhao, G. Zhao, F. Zhang, *Appl. Surf. Sci.* **355** (2015).
- [21] A. Barati, M. Shamsipur, E. Arkan, L. Hosseinzadeh, H. Abdollahi, *Mat. Sci. Eng. C* **47**, (2015).
- [22] A. Mewada, S. Pandey, S. Shinde, N. Mishra, G. Oza, M. Thakur, M. Sharon, M. Sharon, *Mat. Sci. Eng C* **33** (2013).
- [23] X. Guo, C. F. Wang, Z. Y. Yu, L. Chen, S. Chen, *Chem. Commun.* **48**, 21 (2012).
- [24] K. Jiang, S. Sun, L. Zhang, Y. Lu, A. Wu, C. Cai, H. Lin, *Adgew. Chemie* **127**, 18 (2015).
- [25] H. Li, Z. Kang, Y. Liu, S. T. Lee, *J. Mater. Chem.* **22**, 46 (2012).