International Journal of Eco-Innovation in Science and Engineering (IJEISE) Vol 3 (1), 2022 (25-29)
https://ijeise.upnjatim.ac.id/ E-ISSN: 2721-8775

Article

A brief review of C-Dots preparation using top-down and bottom-up approaches.

Nur Aini Fauziyah[1*]

[1] *Department of Chemical Engineering, Faculty of Engineering, Universitas Pembangunan Nasional "Veteran" Jawa Timur (UPN), Gunung Anyar, Surabaya 60294, Indonesia*

*Corresponding author: nur.aini.fisika@upnjatim.ac.id | Phone number: -

Received: 7th February 2022; Revised: 24th March 2022; Accepted: 18th May 2022;
Available online: 19th May 2022; Published regularly: May and November

Abstract

This review paper aimed to reveal several methods that have been used in the preparation of carbon dots (C-Dots). C-Dots were principal to be studied because they have luminous properties that can be used in photocatalyst processes, heavy metal sensors, glowing paints, and nanoparticles for biomedical applications such as bio-tagging. The methods that have been developed were also varied using the two principal approaches, i.e., top-down and bottom-up. Here, we tried to reveal the arc-discharge, laser ablation techniques for top-down approaches, while simple heating methods (simple hydrothermal methods), and microwave for bottom-up. Furthermore, the microwave method was excellent because of the vibration process which caused the carbon chains to undergo rearrangement so that the result was not much reducing the water content in the solution.

Keywords: C-Dots, arc-discharge, laser ablation techniques, simple heating methods, and microwave.

1. Introduction

At present, intensive studies on carbon materials have been published in previous papers [1]–[4]. Carbon material is known as a smart and lightweight material, making it easy to apply in several fields, such as automotive [5], electronics [6], and other advanced materials. Its nanometric size makes carbon materials very famous in various fields.

Carbon is structurally composed of several types of allotropes [7], the most famous of which are graphite, amorphous carbon, and also diamond. Furthermore, the physical behavior of carbon hangs on the type of allotrope. In fact, diamond is transparent, while graphite is black and dull. Diamond is one of the hardest materials in the world, while graphite is quite soft. Diamond, on the other hand, has very low electrical conductivity, and graphite is an excellent conductor of electricity. Based on their shapes, All allotropes of carbon are solid in normal environments, nonetheless, graphite is the most thermodynamically stable allotrope among allotropes. In addition, we can also get nanometric sizes on carbon dots which often

DOI: https://doi.org/10.33005/ijeise.v3i01.54

referred to C-Dots, since they were first discovered in 2004 [8].
Fig. 1. Bottom-up and top-down methods of C-Dots synthesis.

C-Dots are widely known as 0-dimension carbon materials with sizes less than 10 nm [9]. Due to their nanometric size, C-Dots are a very promising new material in various applications. C-Dots are a promising alternative to point quantum-based materials because of biocompatibility [5]. C-Dots were explored as biosensors [10], drug carriers [11], and bioimaging [12] due to their excellent fluorescence properties, biocompatibility, and low toxicity.

In the last few years, there have been many studies describing the synthesis process, its properties, and prospects for future applications, as reviewed by Kelarakis [13], Zuo et al. [14], Anuar et al. [15], and Zaho et al. [16]. Of the many studies that have been conducted, researchers rarely care about the carbon sources used as precursors. So that our focus in this review paper is to thoroughly explore several methods that have been developed in the preparation of C-Dots with bottom-up and top-down methods (see Figure 1). We also cannot specify that in this review paper the carbon sources used are derived from biomass, natural materials, or commercial.

2. Material and Methods

2.1. Top-down methods

a. Arc-discharge

Arc-discharge is one of the top-down methods in the preparation of C-Dots. Many previous researchers have developed this method, one of which was Anuar et al. [15]. He showed that the arc-discharge method was a method of forming C-Dots through rearrangement of carbon atoms that have decomposed from the precursor at the anode through the thrust force of plasma gas produced in a closed reactor. In this condition, the temperature used to reach 4000K below the electric current to produce high energy. While at the cathode there will be an assembly of carbon vapor to form C-Dots, as seen in Figure 2.

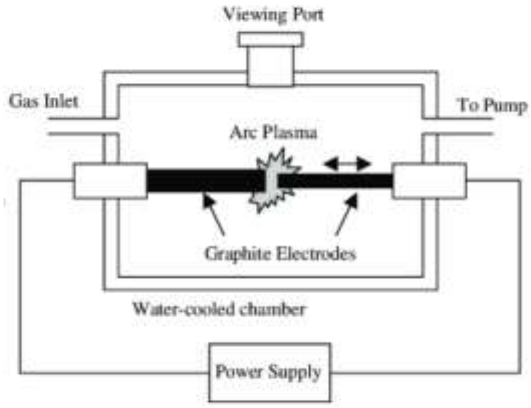

Fig. 2. Arc-discharge in C-Dots preparation [17]

Based on the research of Ge et al. [18] by using arc-discharge, three kinds of nanocarbons were obtained with altered relative molecular masses and fluorescence characterizations. The obtained nanocarbons can emit orange, brown, yellow, and blue-greenmfluorescence colors in the wavelength range of 365 nm. Furthermore, the physical characteristics of the resulting nanocarbon was hydrophilic. The same results were also shown by several other studies [1], [6], [11]. However, the nanocarbon particles produced by Peng et al [11]. This size is still not uniform, some were large (order hundreds of nanometers) and some were below 10 nm. This result still needs to be controlled by the addition of a catalyst or arc-discharge can be carried out in a short time with high energy so that the particles do not clump together and result in agglomeration. In addition, arc-discharge technology is not widely found in all laboratories because it requires high energy and advance equipments. This weakness has been encountered by many previous researchers [19], [20].

b. Laser ablation

Research into laser ablation has a long history. Based on the previous literature [21], the laser ablation method can be explained that when laser heat up to kilo kelvin hits particles, ions, atoms, or groups of atoms, they will interact with the nearby solution and undertake a chemical reaction in the form of cavitation bubbles (see Figure 3). Laser heating requires a very short and fast time, then continues with the cooling process. During the cooling phase, nanoparticles begin to form, and diffuse into the enclosing solution and create a colloidal solution. The complete cycle (heat to cool) needs almost 1 milli second (ms).

DOI: https://doi.org/10.33005/ijeise.v3i01.54

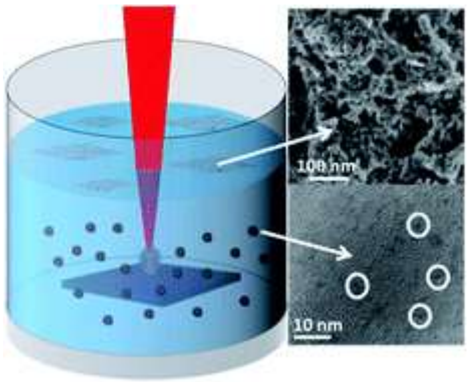

Fig. 3. Laser ablation process in C-Dots preparation [21].

This brief process shows that the production of nanoparticles by laser ablation is very efficient and close to thermodynamic equilibrium. Several researchers have also used this laser ablation method to prepare C-Dots. They were Yu et al [22], Goncalves et al. [23], and Kaczmarek et al. [24]. They used high-energy laser pulses to irradiate the carbon target surface under a thermodynamically developed state of high temperature and high pressure, so that it fast heats up and forms plasma and then haze crystallizes to produce nanoparticles. Indeed, the laser ablation method is one of the valuable method for preparing C-Dots with homogeneous size distribution, and good fluorescence characteristics. Conversely, it need expensive cost and complicated operation.

In general, laser ablation techniques can include three main steps: (1) the carbon material used absorbs high energy by the applied laser pulse; (2) the photoelectric effect which electrons are released from atoms by thermionic emission; and the last is (3) the strong repulsion between the positive ions and the solid material because of high electrical field, so that the carbon material will split into nanometric [21], [25], [26].

2.2. Bottom-up Methods

a. Simple heating method (siple hydrothermal method)

In general, the simple heating method is famous as the simple hydrothermal method. It has a different working step. The sample solution to be synthesized is poured into a container and then the container is tightly closed. The container commonly used is the autoclave. Then the autoclave is put in the oven. The resulting C-dots are in the form of a solution.

Many researchers have synthesized C-dots using the hydrothermal method from various materials. Soni and Maria [27] reported the synthesis of C-dots using carbohydrates. The carbohydrates were dehydrated using sulfuric acid and then treated with HNO_3, to break down the carbon material into smaller carbogenic nanoparticles with a blue shift in emission, but with weak fluorescence. Soni and Maria have been successful to prepared C-dots with 3 nm in size, containing both hydroxyl and carbonyl groups. The procedure for preparing C-dots using the hydrothermal method is as shown in Figure 4.

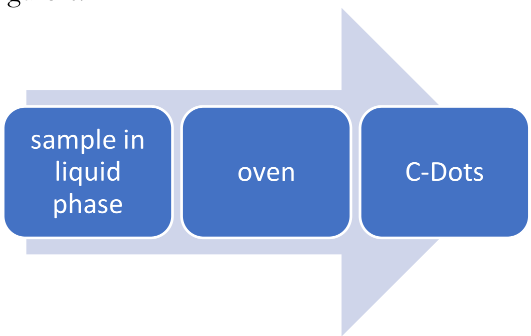

Fig. 4. The simple heating (hydrothermal) procedure for preparation C-dots.

b. Microwave

The microwave method is one of the processes used for the synthesis of C-Dots. The basic principle of this method is the vibration that causes the carbon chains to undergo rearrangement and will produce C-Dots. The advantage of this method is that the sample will not be degraded of the hydroxyl group so that it does not reduce the water content much in the solution. C-Dots synthesized at a low power condition of 70 W.

In general, C-Dots will be synthesized by varying the time the sample is in the microwave. So the result is that the color of the C-Dots synthesis will be different too. Based on previous research [28], the physical properties of C-Dots can be identified from the color. Furthermore, based on the research of Rahmayanti et al. [29], the color characteristics of C-Dots at a synthesis time of 5 minutes, the resulting color was light yellow then the color began to shift to light brown at 35 minutes of synthesis and to dark brown at 45 and 35 minutes of synthesis. This result was in line with the results obtained by Amri et al. [28] where C-Dots were obtained

DOI: https://doi.org/10.33005/ijeise.v3i01.54

from the microwave process and produced a brown color (see Figure 5).

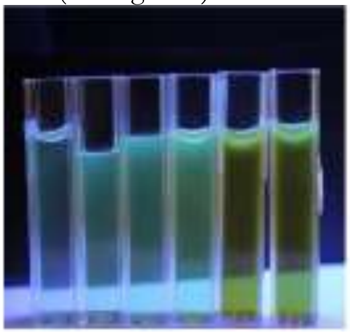

Fig. 5. Characteristics of Luminens C-Dots by microwave method [28].

This color spectrum shows the energy absorption gap in the UV region that electrons jump from the valence band to the conduction band. In addition, the absorption of UV light by C-Dots was observed to be wider by increasing the synthesis time. The synthesis time affects the optical properties of the resulting C-Dots. The lower the energy gap, the lower the energy required to excite electrons from the valence band to the conduction band. This can occur due to the larger size of the C-Dots produced from the heating process. As a result of the increasing number of atoms that make up the particle, the smaller the energy needed to produce electrons that are almost free, meaning the smaller the energy gap width will be.

3. Conclusions

Based on the brief review, it can be seen that the C-dots sample preparation method can be carried out using a bottom-up and top-down approaches. Each method has advantages and disadvantages. Laser ablation and arch-discharge are very effective in preparing C-Dots in a very short time (1 milli second). But in general, using a microwave and simple heating (hydrothermal) methods can also be used to synthesize C-Dots. This method is considered very efficient and does not require advanced equipment.

References

[1] W. Meng, X. Bai, B. Wang, Z. Liu, S. Lu, dan B. Yang, "Biomass-derived carbon dots and their applications," *Energy & Environmental Materials*, vol. 2, no. 3, hlm. 172–192, 2019.

[2] N. Niu *dkk.*, "Preparation of carbon dots for cellular imaging by the molecular aggregation of cellulolytic enzyme lignin," *Langmuir*, vol. 33, no. 23, hlm. 5786–5795, 2017.

[3] M. Tuerhong, X. U. Yang, dan Y. I. N. Xue-Bo, "Review on carbon dots and their applications," *Chinese Journal of Analytical Chemistry*, vol. 45, no. 1, hlm. 139–150, 2017.

[4] J. Yue *dkk.*, "Two-step hydrothermal preparation of carbon dots for calcium ion detection," *ACS applied materials & interfaces*, vol. 11, no. 47, hlm. 44566–44572, 2019.

[5] M. M. Mohideen, Y. Liu, dan S. Ramakrishna, "Recent progress of carbon dots and carbon nanotubes applied in oxygen reduction reaction of fuel cell for transportation," *Applied Energy*, vol. 257, hlm. 114027, 2020.

[6] D. Huang *dkk.*, "Carbon Dots-Decorated Carbon-Based Metal-Free Catalysts for Electrochemical Energy Storage," *Small*, vol. 17, no. 4, hlm. 2002998, 2021.

[7] R. J. Lagow *dkk.*, "Synthesis of linear acetylenic carbon: the" sp" carbon allotrope," *Science*, vol. 267, no. 5196, hlm. 362–367, 1995.

[8] P. Innocenzi dan L. Stagi, "Carbon-based antiviral nanomaterials: graphene, C-dots, and fullerenes. A perspective," *Chemical science*, vol. 11, no. 26, hlm. 6606–6622, 2020.

[9] M. Sharon, N. Mishra, B. Patil, A. Mewada, R. Gurung, dan M. Sharon, "Conversion of polypropylene to two-dimensional graphene, one-dimensional carbon nano tubes and zero-dimensional C-dots, all exhibiting typical sp2-hexagonal carbon rings," *IET Circuits, Devices & Systems*, vol. 9, no. 1, hlm. 59–66, 2015.

[10] J. Wei *dkk.*, "An eco-friendly, simple, and sensitive fluorescence biosensor for the detection of choline and acetylcholine based on C-dots and the Fenton reaction," *Biosensors and Bioelectronics*, vol. 52, hlm. 304–309, 2014.

[11] Z. Peng *dkk.*, "Carbon dots: promising biomaterials for bone-specific imaging and drug delivery," *Nanoscale*, vol. 9, no. 44, hlm. 17533–17543, 2017.

[12] C. Ding, A. Zhu, dan Y. Tian, "Functional surface engineering of C-dots for fluorescent biosensing and in vivo bioimaging," *Accounts of chemical research*, vol. 47, no. 1, hlm. 20–30, 2014.

[13] A. Kelarakis, "From highly graphitic to amorphous carbon dots: A critical review," *MRS Energy & Sustainability*, vol. 1, 2014.

DOI: https://doi.org/10.33005/ijeise.v3i01.54

[14] P. Zuo, X. Lu, Z. Sun, Y. Guo, dan H. He, "A review on syntheses, properties, characterization and bioanalytical applications of fluorescent carbon dots," *Microchimica Acta*, vol. 183, no. 2, hlm. 519–542, 2016.
[15] N. K. Khairol Anuar, H. L. Tan, Y. P. Lim, M. S. So'aib, dan N. F. Abu Bakar, "A review on multifunctional carbon-dots synthesized from biomass waste: Design/fabrication, characterization and applications. Front," *Energy Res*, vol. 9, hlm. 626549, 2021.
[16] A. Zhao, Z. Chen, C. Zhao, N. Gao, J. Ren, dan X. Qu, "Recent advances in bioapplications of C-dots," *Carbon*, vol. 85, hlm. 309–327, 2015.
[17] C. Kingston dan B. Simard, "Fabrication of Carbon Nanotubes," *Analytical Letters*, vol. 36, hlm. 3119–3145, Des 2003, doi: 10.1081/AL-120026564.
[18] G. Ge *dkk.*, "Carbon dots: Synthesis, properties and biomedical applications," *Journal of Materials Chemistry B*, 2021.
[19] F. Richard, J. M. Cormier, S. Pellerin, dan J. Chapelle, "Physical study of a gliding arc discharge," *Journal of applied physics*, vol. 79, no. 5, hlm. 2245–2250, 1996.
[20] A. W. Hull dan I. Langmuir, "Control of an arc discharge by means of a grid," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 15, no. 3, hlm. 218, 1929.
[21] P. Russo, A. Hu, G. Compagnini, W. W. Duley, dan N. Y. Zhou, "Femtosecond laser ablation of highly oriented pyrolytic graphite: a green route for large-scale production of porous graphene and graphene quantum dots," *Nanoscale*, vol. 6, no. 4, hlm. 2381–2389, Jan 2014, doi: 10.1039/C3NR05572H.
[22] H. Yu, X. Li, X. Zeng, dan Y. Lu, "Preparation of carbon dots by non-focusing pulsed laser irradiation in toluene," *Chemical Communications*, vol. 52, no. 4, hlm. 819–822, 2015.
[23] H. Gonçalves, P. A. Jorge, J. R. A. Fernandes, dan J. C. E. da Silva, "Hg (II) sensing based on functionalized carbon dots obtained by direct laser ablation," *Sensors and Actuators B: Chemical*, vol. 145, no. 2, hlm. 702–707, 2010.
[24] A. Kaczmarek *dkk.*, "Luminescent Carbon Dots Synthesized by the Laser Ablation of Graphite in Polyethylenimine and Ethylenediamine," *Materials*, vol. 14, no. 4, hlm. 729, Jan 2021, doi: 10.3390/ma14040729.
[25] G. A. Tafete, G. Thothadri, dan M. K. Abera, "A review on carbon nanotube-based composites for electrocatalyst applications," *Fullerenes, Nanotubes and Carbon Nanostructures*, hlm. 1–9, 2022.
[26] R. Shoukat dan M. I. Khan, "Carbon nanotubes/nanofibers (CNTs/CNFs): a review on state of the art synthesis methods," *Microsystem Technologies*, hlm. 1–17, 2022.
[27] S. Soni dan A. L. Maria, "Luminescent carbon dots: characteristics and applications," *Top Master Nanoscience: University of Groningen*, 2016.
[28] K. Amri dan M. Marpongahtun, "ANALISA MORFOLOGI CARBON DOTS (C-Dots) DARI AIR TEBU," *JURNAL KIMIA SAINTEK DAN PENDIDIKAN*, vol. 5, no. 1, hlm. 6–10, Agu 2021.
[29] H. D. Rahmayanti, M. P. Aji, dan S. Sulhadi, "SINTESIS CARBON NANODOTS SULFUR (C-DOTS SULFUR) DENGAN METODE MICROWAVE," *Unnes Physics Journal*, vol. 4, no. 1, Agu 2015, Diakses: 7 Februari 2022. [Daring]. Tersedia pada: https://journal.unnes.ac.id/sju/index.php/upj/article/view/7009

DOI: https://doi.org/10.33005/ijeise.v3i01.54