We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

5,200 Open access books available
128,000 International authors and editors
150M Downloads

154 Countries delivered to
TOP 1% Our authors are among the most cited scientists
12.2% Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
Chapter

Eco-Friendly Fluorescent Carbon Nanodots: Characteristics and Potential Applications

Adil Shafi, Sayfa Bano, Suhail Sabir, Mohammad Zain Khan and Mohammed Muzibur Rahman

Abstract

Carbon nanodots are zero-dimensional tiny particles of carbon with outstanding characteristics and potential applications. Carbon nanodots are fluorescent materials and possess unique characteristics such as biocompatibility, photostability, low toxicity, sustainable, and eco-friendly. Fluorescent carbon nanodots are emerging nanomaterials that show promising potential in bioimaging, optical sensing, information encryption and storage, photocatalysis, lasers, drug delivery, energy conversion, and photovoltaic applications. Carbon nanodots can be synthesized at very low cost through various sustainable approaches that employ inexpensive renewable resources as starting materials. Carbon nanodots are fascinating carbon-based materials that have received mass attention from past few years for their substantial applications in diverse fields. Carbon nanodots have a huge impact on both health and environmental applications because of their potential to serve as nontoxic replacements to traditional heavy metal-based quantum dots. Herein we highlight the intriguing characteristics and potential applications of fluorescent carbon nanodots in various fields and their perspective in future.

Keywords: carbon nanodots, biocompatible: nanomaterials, health, sustainable

1. Introduction

Carbon nanodots are the emerging class of carbon-based nanomaterials with small size and fascinating properties. Carbon nanodots are surface functionalized carbonaceous nanomaterials with tunable fluorescence and remarkable features [1]. Carbon nanodots are nowadays considered as the rising star in the nanocarbon family due to their sustainable, compatible, cost-effective, and benign nature [2]. Carbon was considered as black material unable to emit light up to the discovery of fluorescent carbon nanodots. The strong tunable luminescence combined with other fascinating properties has attracted considerable attention toward the fluorescent carbon nanodots [3]. Carbon nanodots also called graphene quantum dots share similar properties with graphene oxide with difference in size and shape, as the former is quasispherical in shape with nano-diameters [4]. The promising features of fluorescent carbon nanodots are remarkably assessed in various fields, namely, bioimaging, photocatalysis, optoelectronics, photovoltaics, drug delivery, and sensors [5].
Carbon nanodots were first discovered as a by-product in the purification of single-walled carbon nanotubes [6]. Since then, there have been a considerable increase in the interest of researchers to fabricate carbon-based fluorescent quantum dots, which can substitute the toxic and unstable metallic-based quantum dots (CdS, CdSe, CdTe, PbS, etc.). The fluorescent carbon nanodots possess many advantages over classical quantum dots in terms of biocompatibility, stability, solubility, inertness, cytotoxicity, drug delivery, and synthesis [7, 8]. In addition to that, carbon nanodots do not show photobleaching or blinking effects. In spite of that, they exhibit enhanced quantum yields and strong absorption in the UV-visible region. Although fluorescent quantum dots are prepared from different precursors and synthetic methodologies, the actual mechanism of fluorescence is still in debate [9]. Researchers have reported four possible mechanisms of fluorescence: quantum confinement effect or \( \pi \) domains; the surface state, determined by hybridization of carbon skeleton; the molecular state, determined by surface functionalities; and the crosslink-enhanced emission (CEE) effect [10]. Therefore, the strong blue-green and excitation dependent fluorescence depends on the synthetic method, experimental protocol, and the surface passivation of the carbon nanodot.

From past few years, extensive research is going on fluorescent carbon nanodots because of their intriguing properties and structural functionalities. On the surface of the carbon nanodot, several carboxyl, carbonyl, ammine, and amide moieties are present, which impart excellent solubility and biocompatibility [11]. The surfaces of the carbon nanodots can be modified and passivated with several organic, inorganic, polymer, or biological moieties, which in turn enhance their luminescent, sensing, and other properties. The carbon nanodot doped with a suitable heteroatom shows improved efficiency and enhanced radiative emission due to the shifting of Fermi level [12]. Based on specific surface morphology, carbon nanodots can be hydrophilic or hydrophobic. The hydrophilic nature of carbon nanodots makes them a promising material in diverse fields, thereby attracting the attention of researchers [13].

Among many fascinating applications in diverse fields, photoluminescence is the most researched and at the same time most debated application of these carbon nanodots. Fluorescent carbon nanodots exhibit strong and tunable fluorescence over a wide range of electromagnetic spectrum [14, 15]. Carbon nanodot fluorescence is sensitive to environmental conditions, solvents, temperature, pH, and external agents [16, 17]. Fluorescence is retarded by the agglomeration of particles and enhanced by the dispersion of particles [18]. The tunability of fluorescence provides multicolored blue-green emission, which spans entire visible region and is characterized by increased quantum yield [19]. The fluorescence shown by carbon nanodots can be efficiently quenched by oxidizing or reducing agents in solutions, indicating the electron acceptor or donor capability of carbon nanodots [20]. The redox property of these carbon nanodots can be exploited in light energy conversions, optoelectronics, photovoltaic devices, and in many related applications [21].

Fluorescent carbon dots have been synthesized by different conventional methodologies such as laser ablation, hot injection, hydrothermal, electrochemical, and acidic oxidation methods [22–26]. It is well known fact that carbon nanodots synthesized by different synthetic protocols using different precursors or modifications possess different physiochemical properties, which indicate their complex behavior. However, most methods face some limitation from environmental perspectives in using carbon precursors, synthetic procedure, and purification techniques [27, 28]. At present, extensive research is focused on using natural products to prepare fluorescent carbon dots. Preparation of fluorescent carbon dots by using renewable natural resources is cost-effective and can help in sustainable
development of environment [29, 30]. The eco-friendly synthetic route combined with cost-effective approach can make the synthesized nanodots promising candidates for environmental remediation.

Carbon nanodots with a wide range of possible structures and architectures have been reported. The architecture of both the carbon core and surface functionalities plays a very important role in controlling the activity of the carbon nanodots [31]. The morphology of the carbon dots is nearly quasispherical, but the structure can be graphitic, turbostratic, amorphous, or crystalline. The hybridization of carbon atom may be sp\(^2\) (turbostratic or graphitic carbon) or sp\(^3\) (diamond-like carbon) [32]. In this chapter, the eco-friendly green synthetic approach along with fascinating characteristics and remarkable applications of fluorescent carbon dots is discussed. The surface functionalization and passivation to confer desirable properties to carbon nanodots have been highlighted. The future perspectives and the possible challenges, which can improve the physiochemical properties of carbon dots, have also been discussed.

2. Synthesis of fluorescent carbon nanodots

2.1 Conventional synthesis

Generally, the synthetic procedure of carbon nanodots is quite a tedious process, which involves several steps, surface passivation, and post-synthetic modifications [33, 34]. Also, the physiochemical properties and potential applications of carbon dots solely depend on the synthetic procedures [35]. Two conventional approaches have been employed to synthesize carbon nanodots, top-down approach, and bottom-up approach [36].

Top-down approach involves the cleavage of larger carbon cluster into smaller carbon fragments resulting in the formation of carbon nanodots with diameter less than 10 nm. The large molecules are fragmented by laser ablation, arc discharge, acid oxidation, or exfoliation methods (electrochemical, ultrasonic, solvothermal, and hydrothermal exfoliation methods) [2]. Contrarily bottom-up approach is based on several chemical reactions, which results in the conversion of small carbon precursors into nanoscale carbon dots. In bottom-down approach, the carbon nanodots are synthesized through partial dehydration and dehydrogenation by using microwave, solvothermal, pyrolysis, or thermal decomposition method [37, 38].

During preparation of carbon nanodots, several problems that need to be focused on control of size, proper functionalization of surface, and carbonaceous aggregation should be avoided [39, 40]. Size uniformity is important for uniform properties and mechanistic pathways, whereas surface functionalization is critical for solubility and surface applications. The size or surface properties can be optimized by post-treatment method, such as dialysis, gel-electrophoresis, ultracentrifugation, and filtration. Carbonaceous aggregation can be avoided by adopting electrochemical methods or confined pyrolysis methods [41] (Table 1).

2.2 Green synthesis

The conventional synthesis of carbon nanodots is uneconomical and unjustified because of high cost, tedious experimental protocols, post-preparation modifications, and time-consuming methodologies [45]. Therefore, it is imperative to design facile, eco-friendly, and sustainable methods to synthesize carbon nanodots. Green approach is one of the sustainable methods, which is very easy, cost-effective, eco-friendly, and nonlaborious [46]. From past few years, carbon nanodots were extensively synthesized using natural precursors through greener approach [47].
Carbon-Based Material for Environmental Protection and Remediation

Natural precursors include apple juice, orange juice, shrimps, sweet potatoes, garlic, aloe vera, and honey, which have been utilized as carbon precursors in the preparation of carbon nanodots [48]. In addition to this, plant wastes such as pomelo peel, willow bark, watermelon bark, and waste carbon paper have also been used as carbon precursors for synthesizing carbon nanodots. Biomaterials such as carbohydrates (starch, glucose, and sucrose) have also been utilized for the preparation of carbon nanodots [37]. The replacement of toxic and costly precursors by greener and natural precursors was considered to be the promising method for the synthesis of eco-friendly and potential florescent carbon dots.

2.3 Post-synthetic modifications

The synthesized carbon nanodots can be modified further to obtain nanodots with desirable properties. Generally, two strategies have been applied for post-synthetic modifications: suitable heteroatom doping and surface functionalization or modification.

Heteroatoms such as nitrogen, selenium, and sulfur can be incorporated into the nanodots by using suitable heteroatom-containing precursors [49, 50]. Carbon nanodots have also been co-doped with more than one type of heteroatoms through hydrothermal treatment [51]. Although heteroatom doping is facile method of structure modification, the actual mechanism is still unclear and results in irrational structural design.

Carbon nanodots can be selectively modified with the process of surface modification, which is easily controllable. The surface of carbon nanodots can be functionalized with several reactive intermediates through specific or nonspecific interactions [52]. The functionalization of carbon nanodots results in the tailoring of several properties, which in turn proves beneficial for several potential applications. Carbon nanodots have been passivated with oligomeric polymers to improve fluorescence emissions [53].

<table>
<thead>
<tr>
<th>Synthetic method</th>
<th>Characteristics</th>
<th>Demerits</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser ablation</td>
<td>• Top-down process</td>
<td>Low quantum yield, post-</td>
<td>[42]</td>
</tr>
<tr>
<td></td>
<td>• Fast and effective</td>
<td>treatment is required</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Carbon NDs with strong fluorescence</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>emissions</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Tunable surface states</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical oxidation</td>
<td>• Top-down process</td>
<td>Require drastic conditions, poor</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Most accessible</td>
<td>control over size, poor</td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>• Various sources</td>
<td>control over size, tedious</td>
<td></td>
</tr>
<tr>
<td>Microwave irradiation</td>
<td>• Eco-friendly</td>
<td>Modification not needed but poor</td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td>• Cost-effective and scalable</td>
<td>control over size</td>
<td></td>
</tr>
<tr>
<td>Solvothermal/hydrothermal</td>
<td>• Nontoxic</td>
<td>Poor control over particle size</td>
<td>[43]</td>
</tr>
<tr>
<td>treatment</td>
<td>• Cost-effective and eco-friendly</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrochemical carbonization</td>
<td>• Size control</td>
<td>Small molecule precursors, poor</td>
<td>[44]</td>
</tr>
<tr>
<td></td>
<td>• Stable method</td>
<td>quantum yield</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• One-step method</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Characteristics of different synthetic methods used for preparation of carbon NDs.
3. Morphology and composition

The morphology and structure of the carbon nanodots are exclusively dependent on reaction conditions of synthetic procedures [54]. These nanodots belong to the carbon nano family, existing in several possible substructures. Generally, carbon nanodots are considered to be quasispherical or spherical particles of carbon, which are less than 10 nm in size. The inner core of the carbon nanodots is crystalline or amorphous, but the surface layer covering the core contains several to many functional groups ranging from small amino groups to large fatty acid chains [32]. The crystalline structure of inner core was confirmed by several techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and amorphous nature, which were deduced by HRTEM technique [55]. The inner core is characterized by sp² (turbostratic or graphitic carbon) or sp³ (diamond-like carbon). It has been reported that the inner core can acquire different possible structures at different conditions, particularly at high level of nitrogen doping [56].

The chemical composition of carbon nanodots also varies from one synthetic method to another. The composition of purified carbon nanodots has been reported as 36% carbon, 5.9% hydrogen, 9.4% nitrogen, and 44.7% oxygen. The oxygen content was significantly higher than the carbon nanodot synthesized from raw candle soot (91.7% C, 4.4% O, 1.8% H, and 1.8%N) [57] (Figure 1).

4. Characteristics of fluorescent carbon nanodots

Fluorescent carbon nanodots are tiny particles with fascinating characteristics and commendable properties. These nanodots are considered as versatile carbon members, which show a plethora of applications. In comparison with other semiconductor quantum dots, carbon nanodots show excellent properties, such as [58, 59]

- extraordinary optical, electrochemical, and electronic properties
- tunable fluorescence emission
- less toxicity
- excellent biocompatibility
- chemical robustness
Carbon-Based Material for Environmental Protection and Remediation

- peculiar physiochemical properties
- solubility in water
- multiphoton excitation property
- eco-friendly nature

Carbon nanodots show maximum absorption in UV region with a tail extending to visible region. The optical absorption of carbon nanodots can be shifted to longer wavelength by surface passivation and doping with suitable dopants [60]. It has been observed that the nanodots exhibit size-dependent optical properties ranging from 200 to 500 cm\(^{-1}\), when size is increased from 10 to 21 nm. Moreover, the reactive groups on surface also play a role in increasing the absorption properties of carbon nanodots [60, 61].

Fluorescent carbon nanodots exhibit remarkable wavelength-dependent photoluminescence properties that are totally different from Au nanodots, Ag nanodots, and other metallic nanodots. The fluorescence properties can be tuned through defect states without comprising with core structure. Functionalization of surface removes nonradiative redox recombination centers and increases the quantum yield [62]. Carbon nanodots show multiphoton excitation process, which results in emission of shorter wavelength light than the excitation wavelength. This up-conversion process is a sequential absorption process of one or more photons in the range of 320–425 nm. The photoluminescence from carbon nanodots is possible only when there is quantum confinement of surface energy traps, which becomes emissive upon stabilization through surface passivation [53].

The hydrophilicity of carbon nanodots is because of oxygen-containing functional groups over the surface, which imparts good solubility in water. Hydrophilicity modifies so many properties of carbon nanodots and makes them efficient fluorescent probes for several organic applications [63]. Recently, it has been reported the hydrophilic carbon nanodots can be converted into hydrophobic nanodots by covalent attachment of nonpolar solvents. Hydrophobic carbon nanodots have been used as efficient catalysts in organic synthesis [64].

Carbon nanodots possess remarkable redox properties, which make them efficient photocatalysts for degradation of organic pollutants, oxygen evolution, and CO\(_2\) reduction [65]. The photocatalytic properties are enhanced by heteroatom doping, tuning of bandgap, and interfacial interactions. Carbon nanodots act as a photosensitizer for capturing solar light, thereby facilitating electron-hole separation [66]. Carbon nanodots have shown promising potential in water splitting due to the synergistic effects of several attributes. Zhang et al. introduced the metal-based semiconductor in photocatalysis as carbon dots decorated graphitic carbon nitride photocatalyst for the purification of water by phenol degradation. Muthulingam et al. described about highly efficient degradation of dyes by carbon quantum dots/N-doped zinc oxide photocatalyst and its compatibility on three different commercial dyes under daylight. Sharma et al. introduced about microwave-assisted fabrication of La/Cu/Zr/carbon dots trimetallic nanocomposites with their adsorption against photocatalytic efficiency for remediation of persistent organic pollutants.

4.1 Energy band structure

The energy band structure of carbon nanodots has been proposed on the basis of several computational and theoretical studies. The scheme of energy band structure of inner carbon core and the surface states has been depicted in Figure 2. It is
evident from the figure that carbon nanodots exhibit five emission bands, which have been attributed to electron transitions at intrinsic carbon (305 nm), graphitic nitrogen (355 nm), pyridine nitrogen (410 nm), amino nitrogen (455 nm), and carboxyl carbons (500 nm) [67].

5. Applications

Fluorescent carbon nanodots have emerged as versatile carbon nanostructures with a wide range of potential applications. Based on their intriguing and fascinating properties such as biocompatibility, water solubility, and high stability, they are utilized as favorable materials in diverse fields. Carbon nanodots are promising materials and find substantial applications in bioimaging, photocatalysis, sensors (biosensors and chemical sensors), drug delivery, energy conversions, supercapacitors, LEDs, and many related processes [32, 68, 69]. In addition to this, carbon nanodots have shown great achievements in the field of food science in terms of food safety, nutrient management, and food toxicity [70–81]. The surface functionalizations with suitable reactive moieties have rendered carbon nanodots efficient in several biomedical applications such as in vivo and in vitro fluorescent probes and biomarkers. The applicability of carbon nanodots in biological and chemical sensing shows excellent results with respect to sensitivity, selectivity, stability, reproducibility, and response time.

5.1 Sensing

Carbon nanodots have been utilized as novel, efficient, and environment friendly fluorescent probes for the detection of trace quantities of chemical and biological analytes. Due to their fascinating and useful properties, carbon nanodots have been employed as biosensors for monitoring of glucose, DNA, phosphate, potassium, nitrite, and cellular copper with high selectivity and sensitivity [77, 82, 83]. The photoluminescence properties of carbon nanodots were investigated for the detection of various solvents (VOCs) [84]. It was reported that cyclic voltammetry technique was employed for selective and sensitive detection of glucose by using nitrogen-doped carbon nanodots with a LOD of 1–12 mM [85]. Boron-doped carbon nanodots were effectively utilized as chemosensors for trace detection of hydrogen.
Peroxide and glucose with very low detection limit [86]. Moreover, metal-doped carbon nanodots were effectively used as fluorescent sensors for sensing of dopamine, amoxicillin, catechol, pyridine, formaldehyde, pyrene, and so on [87, 88]. Metal-doped carbon nanodots have shown a considerable role in pH and temperature sensing in aqueous systems. Metal ions like Fe$^{3+}$ are very important for the metabolism of living beings, and any fluctuation in its routine can be disastrous for human beings. Carbon nanodots can help in the detection of fluctuation of Fe$^{3+}$ and thereby help in maintaining stable iron metabolism in the body [89].

Carbon nanodots can be used as a fluorescent nanosensor for nucleic acid detection with single-base mismatch [90–93]. The sensing is based on the adsorption of fluorescent labeled single-stranded DNA over carbon nanodots followed by fluorescence quenching and subsequent hybridization with its target to form double-stranded DNA (Figure 3).

5.2 Photocatalysis

Due to efficient redox properties, carbon nanodots have been efficiently employed as photocatalysts for harnessing solar energy in organic pollutant degradation. Carbon nanodots upon irradiation generate electron hole pairs, which can be subsequently utilized for multiple applications in pollutant degradation, CO$_2$ reduction, and photo catalytic water splitting [94, 95]. Carbon nanodots have been considered as excellent photocatalysts with a strong absorption in the wide range of electromagnetic spectrum. However, due to poor electron transfer inside the carbon nanodots, the application has been impeded. In order to increase the efficiency of carbon nanodots and to make them better photocatalysts, their electronic structure is modified by adopting several strategies namely, metal ion doping, heterostructure formation, composite formation, and so on [8, 95]. Doped carbon nanodots show efficient electronic properties with a strong visible light absorption and show low recombination of charge carriers [96]. Nitrogen-doped carbon nanodots in comparison with bare carbon nanodots show efficient visible light photo catalytic degradation of methyl orange. It has been also reported that carbon nanodots in the size range of 1–4 nm showed good photocatalytic oxidation of benzyl alcohol to benzaldehyde in the presence of H$_2$O$_2$ [97]. The conversion efficiency under NIR light was observed to be 92–100%, confirming better redox properties of carbon nanodots. The proposed mechanism for the conversion has been demonstrated in Figure 4.
5.3 Optronics

White light emitting diode can help in saving a lot of energy, but conventional diodes with rare earth metals suffer a drawback in terms of cost, stability, and toxicity. Because of low cost, eco-friendliness, high-quantum yield and low toxicity, carbon nanodots are replacing the traditional white light emitting diodes. Carbon nanodots are the promising materials to replace phosphors in white light emitting diodes with toxic elements such as cadmium and lead [98]. Carbon nanodots serve as a potential candidate in dye-sensitized solar cells, supercapacitors, and organic solar cells [99, 100]. Carbon nanodots doped with nitrogen or coupled with polymer matrix show a considerable attention in LEDs because of flexibility, thermal stability, and robustness.

6. Conclusion

In summary, fluorescent carbon nanodots are the members of carbon family with fascinating and remarkable properties. Although several protocols have been discussed about their synthesis, the size control and precise morphologies have not been attained yet. It is noteworthy to mention that the green synthesis of carbon nanodots has proved facile and effective in controlling the size and properties. Fluorescent carbon nanodots are unique tiny materials with extraordinary characteristics and commendable properties. The properties of carbon are explored in several fields. Carbon nanodots have shown explicit potential in biomedical, photovoltaic, optoelectronic, and electrochemical fields. In addition, the excellent redox properties and light harnessing potentiality have rendered them potential candidates for photo catalytic applications. Furthermore, the newly discovered chroptical properties of carbon nanodots will certainly find promising applications in both biomedical and electronic fields. Despite of the peculiar and remarkable applications in diverse fields, several properties of the carbon nanodots are still unclear. In future, extensive studies are needed to elucidate the possible mysteries and novel applications of carbon nanodots.
Acknowledgements

The authors are highly thankful to the Department of Chemistry, Aligarh Muslim University for providing research facilities. The authors also acknowledge the authors whose work in the form of images has been reproduced in this chapter.

Author details

Adil Shafi¹, Sayfa Bano¹, Suhail Sabir¹, Mohammad Zain Khan¹ and Mohammed Muzibur Rahman²*

1 Environmental Research Laboratory, Department of Chemistry, Aligarh Muslim University, Aligarh, India

2 Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia

*Address all correspondence to: mmrahman@kau.edu.sa; mmrahmanh@gmail.com

IntechOpen

© 2020 The Author(s). Licensee IntechOpen. Distributed under the terms of the Creative Commons Attribution - NonCommercial 4.0 License (https://creativecommons.org/licenses/by-nc/4.0/), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited.
Eco-Friendly Fluorescent Carbon Nanodots: Characteristics and Potential Applications

DOI: http://dx.doi.org/10.5772/intechopen.89474

References


Chemical Communications. 2010;46(21):3681-3683


[33] Zhu S et al. Surface chemistry routes to modulate the photoluminescence of graphene quantum dots: From


[38] Lecroy GE et al. Toward structurally defined carbon dots as ultracompact fluorescent probes. ACS Nano. 2014;8(5):4522-4529


Eco-Friendly Fluorescent Carbon Nanodots: Characteristics and Potential Applications

DOI: http://dx.doi.org/10.5772/intechopen.89474


[87] Li H et al. Fluorescent N-doped carbon dots for both cellular imaging and highly-sensitive catechol detection. Carbon. 2015;91:66-75


