Indian Journal of
Advances in Chemical Science

Article

# Recent Advances in the Green Synthesis of Carbon Dots and their Applications

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**ABSTRACT**

Carbon dots have emerged as extremely useful material in the recent era because of their excellent physicochemical properties, extremely small size, economical synthesis, biocompatibility, and low toxicity levels as compared to other zero-dimensional materials. Their method of synthesis involves both top-to-down and bottom-to-up approaches such as laser ablation, thermal ablation, chemical oxidation, and sonochemical and electrochemical methods. However, the green synthesis of carbon dots has grabbed much attention owing to its low cost and eco-friendly approach. Green synthesis of carbon dots is not only useful for lowering the toxicity of synthesized nanoparticles but also helps in mitigating bio-waste that lands up in landfills without undergoing the process of biodegradation. They have a wide variety of applications that include catalysis, biomedicines, sensing, and imaging applications. In the present communication, the green synthesis of carbon dots has been highlighted along with their applications in various fields.

**Key words:** Applications of carbon dots, Carbon dots, Green synthesis, Methods of synthesis

## 1. INTRODUCTION

Carbon dots are zero-dimensional nanomaterials of the carbon family with tunable physical, chemical, and optical properties having sizes <10 nm and were first reported in 2004 by Xu *et al.* [1]. They are composed mainly of $sp^2$ hybridized carbon along with some amorphous carbon regions. Owing to their excellent properties such as tunable fluorescence, high solvent solubility photoluminescence, chemical inertness, biocompatibility, easy functionalization, broad excitation spectra, and resistance to photobleaching [2-4]. The two basic approaches exploited for the synthesis of carbon dots include top-down and bottom-up approaches. The top-down approach includes breaking or grinding graphite oxide sources into nano-sized carbon dots which initially involves the conversion of graphene into graphite oxide using harmful chemicals [5]. The bottom-up approach involves carbonization and polymerization of smaller carbon units to form carbon dots. Recently, plants and microorganisms are being used for the synthesis of carbon dots as they are renewable, eco-friendly, efficient, inexpensive, and less toxic sources. Some of the examples of the green sources that have been used for the synthesis of carbon dots include *Eleocharis dulcis, Azadirachta indica*, Maize, Rose-heart radish, *Ocimum sanctum, Tamarindus indica, Allium fistulosum, Abelmoschus manihot, Osmanthus fragrans* [6-14]. Green synthesis is named so because of the principles involved such as the use of safer and less toxic chemicals for the synthesis, energy efficient reactions, use of renewable resources, and safer solvents as the medium. Furthermore, the product formed should be of low toxicity and stable chemically. The ability to acclimatize the properties has opened ways for a variety of applications including sensing [15], photoelectronics [16], phototherapy [17], antibacterials[18], photocatalysis [19] and bioimaging [20]. The useful properties of carbon dots have been represented in Figure 1.

This review summarized the synthesis of carbon dots through various methods, their merits demerits, sizes, optical properties, and composition that find application in various applications.

## 2. GREEN SYNTHESIS OF CARBON DOTS FROM DIFFERENT SOURCES

Carbon sources used for the synthesis of carbon dots can be synthetic as well as natural. Conventional bottom-up and top-down create a haphazard environment as they involve the use of large amounts of unsafe solvents, toxic precursors, expensive raw materials, and high energy input. However, green synthesis put an end to the demerits by overcoming the flaws of conventional techniques of synthesis. The following are some sources that act as precursors in the synthesis of carbon dots.

### *2.1. Biomass*

Agricultural wastes, animal wastes, municipal wastes, industrial wastes, and forest and fisheries wastes contain a biodegradable fraction that is referred to as biomass. The use of biomass has significantly risen in the recent era because of its multidisciplinary use and because of its sustainability. Biomass comprises carbohydrates, polyphenols, carotenoids, alkaloids, terpenoids, proteins, etc. Mewada *et al.* synthesized biocompatible carbon dots using *Trapa bispinosa* peel of sizes ranging from 5 to 10 nm with prominent green fluorescence when observed under ultraviolet (UV) light [21]. Cheng *et al.* synthesized carbon dots from carbonized walnut shells having a size of about 3.4 nm and showed green fluorescence under UV light [22]. Atchudan *et al.* synthesized carbon dots with nitrogen doping of size 5 nm

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**ISSN NO:** 2320-0898 (p); 2320-0928 (e)
**DOI:** 10.22607/IJACS.2023.1104006

**Received**: 12th October 2023;
**Revised:** 24th November 2023;
**Accepted:** 26th November 2023

from *Chionanthus retusus* extract using hydrothermal carbonization. Transmission electron microscopy (TEM) images of these nitrogen-doped dots show that the interlayer distance was 0.21 nm and exhibited high fluorescence properties, low cytotoxicity, and high selectivity toward Fe(III) ions [23]. Similarly, green synthesis of carbon dots was carried out for sensing silver ions using broccoli hydrothermally with prominent blue fluorescence. The blue fluorescence of the synthesized dots was considerably quenched when combined with silver ions thus detecting it [24]. Apple juice-mediated green synthesis of carbon dots was utilized in the detection of mercury ions by codoping it with nitrogen and sulfur by Yue *et al.* Mercury ions are one of the most fatal ions when it comes to human ingestion and interaction. TEM images of these carbon dots show their size around 2.8 nm along with the presence of graphitic $sp^2$ carbon [25]. These carbon dots from apple juice had better efficiency when compared to the quantum dots composed of amalgamated carbon dots such as CdS and CdTe. The synthesized particles were put to test for the degradation of various hazardous dyes such as Eriochrome Black T, methyl orange, acid blue, eosin Y, and acid red dyes and were found to be efficient for degradation [26].

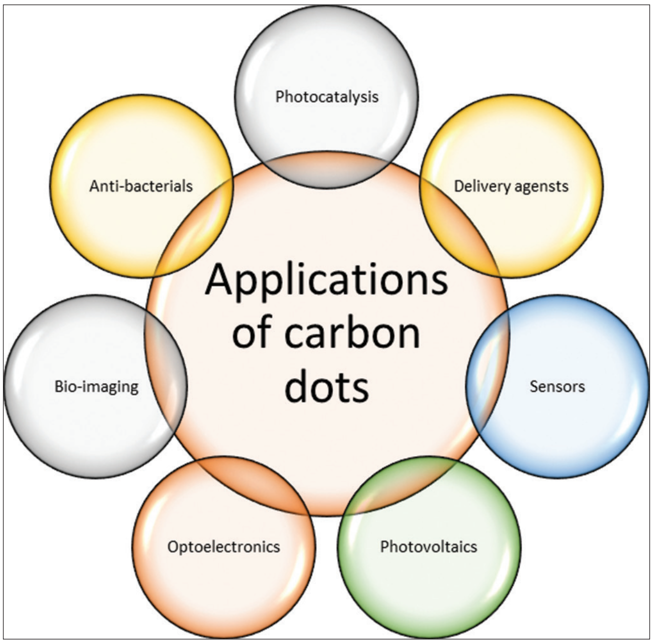


**Figure 1:** Useful applications of carbon dots.

### *2.2. Microorganisms*

The use of microorganisms for green synthesis of metal and metal oxide nanoparticles has thrived on a large scale as they prove to be energy efficient, eco-friendly, fast, waste reducing, and safe alternatives to hazardous chemicals. Majorly used microorganisms for the synthesis of carbon dots include bacteria, algae, and fungi. Bacteria-mediated synthesis of carbon dots embraces *Bacillus cereus, Lactobacillus plantarum.* One-step hydrothermally synthesized carbon dots from *Bacillus cereus* were used for the detection of p-nitrophenol with a sensitivity of 0.11 μM and also exhibited excellent photostability, high biocompatibility, and fluorescence with multicolor [27]. In another study, *Lactobacillus plantarum* was used for the synthesis of fluorescent carbon dots that have remarkable application in the treatment of biofilm [28]. Apart from bacterial synthesis, algal synthesis of carbon dots has also been studied and the algae precursor was found to play a crucial role in the crystallinity, fluorescence, and composition of the carbon dots. The algal precursors for the synthesis of carbon dots include *Nannochloropsis,* Dunaliella salina, biochar, etc. *Saccharomyces cerevisiae* yeast was used for the synthesis of carbon dots which were excellent probes for the detection of manganese(VII) ions and L-ascorbic acid in the test water sample and herbs sample.

### *2.3. Bioactive Molecules*

Bioactive molecules serve as an important precursor for the synthesis of carbon dots as establish better conditions required for the process and produce particles with better properties. Alanine and ethylene diamine molecules were used for the synthesis of carbon dots with an average diameter of 8 nm using the process of hydrothermal carbonization. These resultant particles were known to have good biocompatibility, low cytotoxicity, and act as sensitive detectors

**Table 1:** Sensing applications of carbon dots.

| Precursors | Synthesis method | Size | Sensed ion and molecule |
|---|---|---|---|
| Fish scales | Hydrothermal | <10 nm | $Fe^{3+}$ions |
| Shrimp shells | Calcination | <10 nm | $Cr^{6+}$ions |
| Prawn shells | Hydrothermal | 4 nm | $Cu^{2+}$ions |
| Palm shell powder | Hydrothermal | <10 nm | Nitrophenols |
| Pineapple peel | Hydrothermal | <10 nm | $Hg^{2+}$ions |
| Sugarcane bagasse | Ultrasonic wet chemical oxidation | <10 nm | $F^-$ ions |
| Lemon peel | Hydrothermal | 1–3 nm | $Cr^{6+}$ions |
| Apple seeds | Pyrolysis | <10 nm | 4-nitrophenol |
| Waste tea extract | Hydrothermal | <10 nm | $CrO_4^{2-}$, $Fe^{3+}$ions |
| Oil palm empty fruit benches | Hydrothermal | 3.4 nm | $Cu^{2+}$ions |
| Rice husk | Thermal carbonization | <10 nm | $Sn^{2+}$, alcohol vapors |
| Spoiled milk | Hydrothermal | <10 nm | $Cr^{3+}$ions, $Cr^{6+}$ions |
| Spent coffee grounds | Solvent free carbonization | 2.1–3.9 nm | $Fe^{3+}$ions |
| Citric acid, urea, thiourea | Microwave | <10 nm | $I^-$, $Hg^{2+}$, uric acid |
| Ethylene diamine tetraacetic acid | Solvothermal | <10 nm | $Fe^{3+}$, apoferritin |
| Hyaluronic acid | Hydrothermal | <10 nm | $Fe^{3+}$, folic acid |

**Table 2:** Precursors, size, synthesis methods, and their application in bioimaging.

| Precursors | Synthesis method | Size | Application |
|---|---|---|---|
| Citric acid and cystamine dihydrochloride | Hydrothermal | 1.3–2.3 nm | HeLa cells detection |
| Albumin | Hydrothermal | <10 nm | Human breast cancer Bcap-37 cells detection |
| Grapefruit peel | Hydrothermal | <10 nm | p53 protein detection |
| Lychee exocarp | Hydrothermal | <10 nm | Cancer cells probe |
| Mango peel | Pyrolization | 2–6 nm | Cellular labeling of A549 cells |
| Pseudo stem of banana plant | Hydrothermal | <10 nm | Imaging of MCF-7 and HeLa cells |
| Peanut shells | Hydrothermal carbonization | <10 nm | HepG2 cells imaging |
| *Allium fistulosum* | Hydrothermal | 4.22 nm | MCF7 and K562 cells |
| Watermelon peels | Carbonization | 2 nm | HeLa cells |

**Table 3:** Catalytic application of carbon dots synthesized from various precursors.

| Precursor | Synthesis method | Size | Application |
|---|---|---|---|
| Bitter Apple peels | Charring | <10 nm | Photodegradation of crystal violet |
| Orange waste peels | Hydrothermal carbonization | <10 nm | Photocatalyst for degradation of naphthol and azo dyes |
| Coffee grounds | Carbonization | 3–4 nm | Redox reaction catalyst |
| Apple juice | Carbonization | <10 nm | Photodegradation of Eriochrome Black T, methyl orange, acid red, acid blue, methyl blue dyes |

for dihydronicotinamide adenine dinucleotide [29]. Similarly, biomolecules such as D-glucose, L-aspartic acid, adenosine disodium triphosphate, adenosine, cytidine, thymidine or guanosine, aspirin, jiosanxian, citric acid, procaine, citric acid, ethylenediamine, curcumin, vancomycin, and aminosalicylic acid were also used for the synthesis of carbon dots.

### 2.4. Waste Materials

The synthesis of carbon dots from waste materials has the added advantage of minimizing the wastes that linger in the environment and creating a hazard in the environment. Waste materials like clotted cream were used to synthesize carbon dots coated with Pd nanoparticles. Sewage sludge upon microwave irradiation leads to the synthesis of carbon dots with a quantum yield of about 21.7% with sensitive detection of paranitrophenol with an average diameter of 17.5 nm [30]. Waste black toner ink, paper, kerosene fuel soot, candle soot, polyethylene terephthalate. Polystyrene, polypropylene, polyurethane, and polyacrylamide are some other examples from which carbon dots have been synthesized.

## 3. APPLICATION OF CARBON DOTS

### 3.1. Sensors

Carbon dots prove to be excellent sensors for metal ions, bioactive molecules, and some dyes. The sensing ability of carbon dots is based on the quenching of their photoluminescence on contraction with the molecule to be detected which can easily be observed in their fluorescence spectra. A summary of the nanoparticles that have been used as sensors for various molecules and ions is mentioned in Table 1.

### 3.2. Bioimaging

Owing to excellent biocompatibility, low cytotoxicity, and photobleaching resistance of green synthesized quantum dots, it is used as a probe for imaging applications. Some carbon dots exhibit multicolor fluorescence which is better for imaging purposes by letting users switch between different fluorescent wavelengths using only a solo type of carbon dots. The carbon dots can be used as both *in vivo* and *in vitro* probes. It helps in the early detection of cancerous tumors, cancerous cells, and other critical illness conditions. Therefore, helping humankind by early detection-early medication approach. A summary of different types of carbon dots used for imaging different types of cells is mentioned in Table 2.

### 3.3. Catalysis

Carbon dots have a high surface-to-volume ratio and their tunable functionalization makes them an efficient catalyst for various reactions. Willow bark-mediated synthesis of carbon dots finds applications as a photocatalyst for the reduction of Au nanoparticle and graphene oxide nanocomposite formation. The nanocomposite was also used for catalyzing the reaction of glucose and oxygen converting them into hydrogen peroxide [31]. Some other green synthesized carbon dot sources, sizes, and applications as a catalyst are summarized in Table 3.

### 3.4. Biomedicine

Carbon dots are known to show exceptional properties because of the ease of functionalization which allows the target to be approached actively. Carbon dots with hollow morphology with an average diameter of 6.8 nm were synthesized by Wang *et al.* and loaded with doxorubicin-HCD complex to observe the red fluorescence emitted from the cell when the nucleus of A549 cells was approached [32]. The process helped in understanding the entry mode of the drug in the cell through endocytosis, which releases the doxorubicin-HCD complex on encountering lower pH lysosomes. Similarly, it was studied that carbon dots synthesis from leaves of the mulberry plant can be loaded with the anti-cancer drug lycorine which showed enhanced cell mortality of cancerous HepG2 cell line as compared to the drug alone [33]. Antibacterial activity of henna leaves synthesized carbon dots was seen against *Staphylococcus aureus* and *E. coli* bacteria [34].

## 4. CONCLUSION

Through the above study, we have described the recent trends in the green synthesis of carbon dots, and the applications of green synthesized carbon dots in various fields making it viable for large-scale implementation to lower the impact on the environment and replace the conventional methods of synthesis which are toxic, energy inefficient, slow, waste producing, expensive, and time-consuming. Carbon dots are an assorted class of nanomaterials with a number of decipherable pathways of production which can improve their properties so that their applications can be advanced to other fields as well.

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