

An Investigation on Synthesis of Carbon Dots, its Photoluminescence property and the various applications

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Abstract: Carbon dots (CDs) is a much explored new class of material developing now-a-days for a wide variety of applications due to their promising properties of fluorescence, simple synthetic approaches, good biocompatibility and various detection applications. The demand for green chemistry and cost-effectiveness leads to synthesize C-dots from natural sources. Nanometre sized carbon dots with unique optical properties of great importance due to its interesting wide applications. Natural Carbon Dots and Nitrogen doped carbon dots (N-CDs) were prepared from Natural sources by hydrothermal method. The CDs giving good water dispersibility, strong blue fluorescence emission colour provide an excellent photo and pH stabilities. The fluorescence of CDs is resistant to the interference of biomolecules, metal ions and high ionic strength. Carbon dots with less than 100nm sizes have been as a fascinating tool in sensing and bioimaging. Carbon dots can be naturally extracted from various parts of plants like flowers, leaves, seeds etc. This review presents the current progress in the development of CDs with an emphasis on Synthesis methods, fluorescent properties and applications in sensing, imaging and catalysis.

Key Words: Carbon dots, natural sources, sensing, bioimaging, photo catalysis, photoluminescence etc.

1. Introduction

Carbon dots (CDs) are the latest promising nanomaterials that have been received a high degree of appreciation in various fields due to its major outstanding properties such as due their easy availability, cost-effectiveness, thermal stability and relatively cytotoxic nature. [1]. Carbon dots, the latest allotrope of carbon is the latest generation of small carbon nanoparticle, which exhibits photoluminescence properties [2]. Carbon dot in combination with other materials like natural polymers produces a composite material of enhanced strength with widened applications. The CDs have been produced from various carbonaceous materials like graphene, graphite and carbon nanotubes by physical methods like electrochemical oxidation and thermal oxidation [3]. Such carbon dots have been distinguished as excellent fluorescent materials for different potential applications including biomedical imaging, photo catalyst and optoelectronic devices [4]. Carbon dots are mainly composed of non-toxic C, O and N, and are considered being biocompatible and these elements are mainly obtained from the natural sources [5]. C-dots are of more interest compared to established quantum dots, as they are considered nontoxic and low cost effective [6]. Although CDs have been explored extensively, it still remains a challenge to explore more of it because of their complex chemical structure [7].

Various approaches involving electrochemical synthesis, microwave/ultrasonic preparation, hydrothermal/acidic oxidation routes, and arc-discharge, laser-ablation and plasma treatments have been developed to fabricate CDs. In

most cases, CDs were formed from the precursors of fine carbon structures (like graphene and carbon nanotubes or conventional chemicals such as citric acid monohydrate, carboxylates and carbohydrates. Recently approach has been achieved by utilizing natural bio based resources as starting materials, such as gas soot, soybeans, orange juice etc. [8,9, and 10].The sources for CDs can be either man made (e.g., candle soot, fullerene C60, graphite, polyethylenimine and ammonium citrate) or natural sources (e.g. milk, juice, coffee grounds, green tea, egg, flour, potato, hair, garlic, flowers,, seed powders, leaves) [11].Firstly, natural products are renewable and have good biocompatibility. Secondly, the natural products contain heteroatom, which infect facilitates the fabrication of heteroatom doped CDs without the addition of an external heteroatom source. [11].The general term “carbon-dots” is commonly used for fluorescent carbogenic materials with an external shell composed of carboxylic or other chemical functional groups and an internal graphitic core eventually containing covalently bond oxygen and nitrogen atoms [12,13].

The structure of carbon dots enhances the optical properties. The emission character of carbon dots changes depending on their size because of quantum confinement effects. Decrease in the size of carbon dots shifts the emission colour to the blue region and increase in size of carbon dots shifts the emission colour to yellow, green or red light. The optical properties of carbon dots can be further increased by Heteroatom doping or surface passivation [14].

Carbon dots show polar nature and can be easily customized due to the presence of various functional groups on their surfaces such as hydroxyl, carboxyl, ester or amine. Carbon dots can be synthesized according to Green Chemistry principles without using toxic reagents [15, 16].

In today's trend attempt is being made on self-passivation of carbon dots by hydrothermal carbonization at high temperature or microwave assisted hydrothermal carbonization. All these methods have from some imperfection like the requirement of complex and time consuming process, a high temperature and synthetic conditions, hence these methods limits their wide applicability [17-20].Carbon dots have been acknowledged as separate quasi-spherical particles with sizes below 100nm and them generally posses a sp^2 conjugated core and contain suitable oxygen content. Carbon dots have also favourable properties including simplicity of production and chemical characterization, large packing capacity, lack of immunogenicity, and potential for tissue specificity [21, 22]. The most leading feature of carbon nanodots to other carbon nanomaterials is that those CDs can be produced in multi-gram scale simply by heating natural sources [23-25].

2. Synthesis methods of CDs

There are basically two methods for the preparation of CDs top-down method and bottom-up method [11].In “top-down” method, CDs are generated from relatively micro carbon sources and mostly from natural products including fruit, biomass materials and waste products can be used for the preparation of CDs [11].In “bottom-up” method, precursors are required as seeds are grown into CDs and this method is suitable for the preparation of CDs from natural sources [11]. Fig 1 shows the general preparation methods of carbon dots [4, 11].Fig 2 shows the Top-down and Bottom-up approaches for the synthesis of CDs [4,11,14].

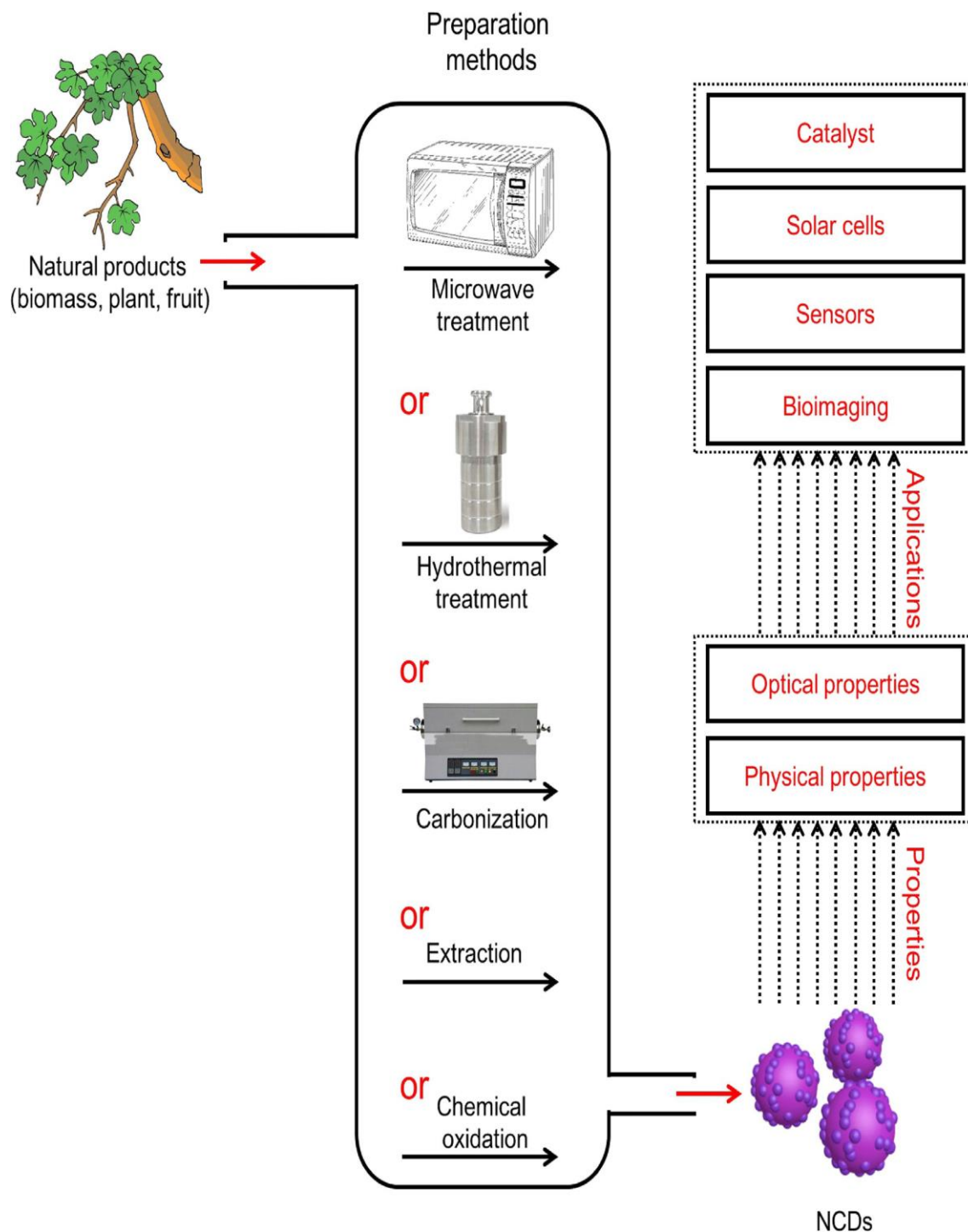


Fig 1 General preparation method for CDs

2.1. Top-down method

Fanglong Yuana et al synthesized fluorescent CDs by the top-down method through laser ablation of graphite using argon as a carrier gas in the presence of water vapour [13]. The approaches towards synthesis of CDs were developed by increase the size of graphite, graphene or graphene oxide(GO) sheets, carbon nanotubes (CNTs), carbon fibers, carbon soot and other materials which possess a perfect sp^2 carbon structure and lack an efficient band gap to give fluorescence [11]. For top-down approaches, many methods are developed to break down the carbon structure into CDs such as arc discharge ,laser ablation, nanolithography by reactive ion etching (RIE) ,electrochemical oxidation , hydrothermal or solvothermal , microwave assisted , sonication assisted and chemical exfoliation [11].

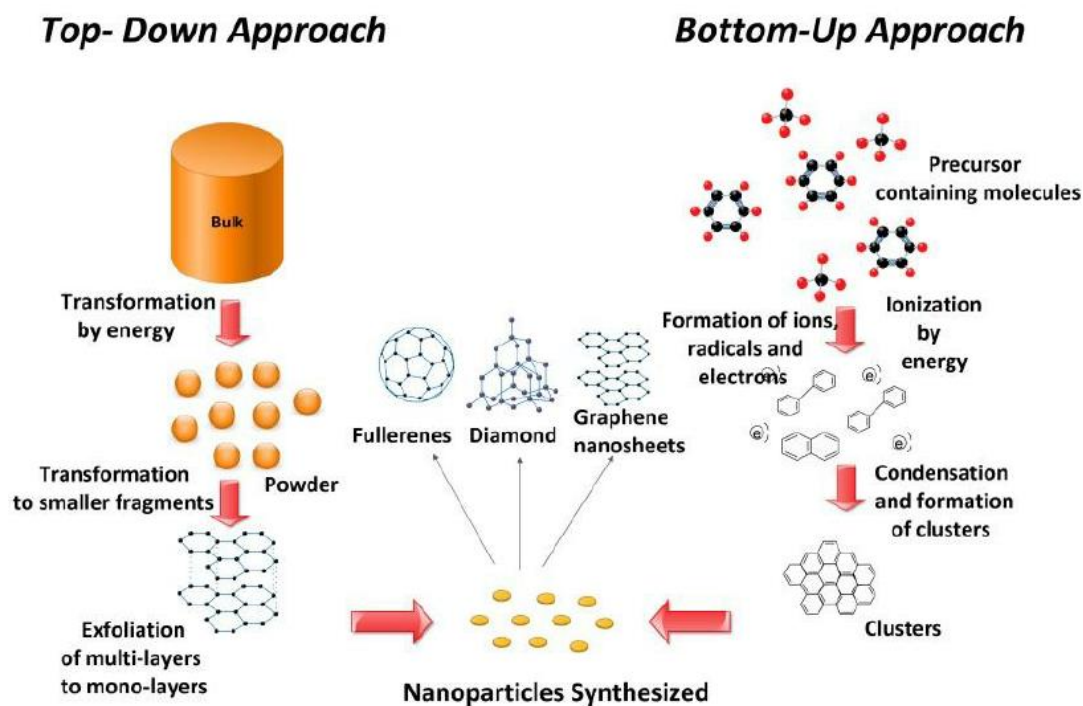


Fig 2 Top-down and Bottom-up approaches for the synthesis of CDs

2.2. Bottom-up method

The bottom-up methods offer exciting opportunities for controlling the properties of CDs with well-defined molecular weight and size, shape and properties by using elaborately designed pre-cursors and preparation processes [11]. The bottom-up methods are obtained from low-cost and quite efficient for producing fluorescent CDs on a large-scale, a prerequisite for practical applications of these novel CDs [13]. This synthetic method could restrict the particle size to smaller than 100 nm and afford an appropriate chemical composition of CDs for a tuneable emission with a relative high fluorescence [11, 13]

3. Photoluminescence mechanism of CDs

One of the most interesting properties of CDs is their tuneable photoluminescence (PL) due to their surface effects and large rigid conjugated structure. Differently colour CDs have been synthesized with different approaches, ranging from deep ultraviolet to red or even NIR emission and most commonly blue and green [13,24]. In general, the PL spectra of CDs are almost symmetrical on the whole wavelength scale. The fluorescence spectra are usually broad due to the wide dot size distribution to say, the excitation-dependent PL behaviours of CDs are highly promising for imaging applications [26].

Soon after the discovery of CDs in 2004, researchers began to investigate regarding the PL of CDs [26]. Three main theories explain the PL is quantum confinement, molecular state, and surface state [27]. Another common theory suggests that the different molecular fragments which are attached to the surface of CDs induce PL [28]. Several CDs involved with Citric acid as a source is based on the molecular state theory [29]. Additionally, there have been some studies, which used a fluorescent precursor in the preparation method, to explain their CDs PL using molecular state [30]. These claimed the precursor fragment is on the surface of CDs. While there are strong evidence for this theory in some CDs systems. The third most common theory is the surface state-controlled PL [31]. The frequent use of this explanation has caused the general acceptance of this theory for the PL mechanism of CDs [32].

many of the anion assays are based on the fluorescence enhancement (fluorescence recovery) of the already quenched CQD–metal complexes. For example, in the I⁻ assay, the fluorescence of the CQDs was recovered due to the formation of more stable complexes between I⁻ and the metal ions, displacing the CQDs in the CQD–metal complexes [39]. It is well known that, a wide variety of procedures and a large number of starting materials have been used in the preparation of CDs which lead to the variation in fluorescence characteristics and are strongly dependent on the composition of CDs and the residue chemical groups on their surface. Therefore Standardization is required for the preparation of CDs and to assess the property of PL to evaluate the performance of CDs

4.2. Bio Imaging

C-dots are a greener alternative for bio imaging due to their high PL, biocompatibility, low toxicity, as well as chemical and photo stability. Other metal nanoparticle such as silver and gold have been demonstrated to be a safer alternative for the purpose of bio imaging, but they are too expensive and also they lack good photo stability [20]. C-dots from coffee ground were used for imaging LLC-PK1 cells, showing that the C-dots were localized in the cell membrane and cytoplasm through endocytosis [40]. C-dots prepared from green tea were used for both imaging and inhibiting the growth of cancer cells such as MCF-7, MDA-MB-231, LLC-PK1 and HeLa cells [41]. Fig 4 shows the Cell images obtained by Hsu et al. showed that CQDs are mostly localized in the cytoplasm and cell membrane. It was also shown that water-soluble CQDs passivity with PPEI-EI could label the cell membrane and cytoplasm of MCF-7 cells and they do not reach the nucleus [42].

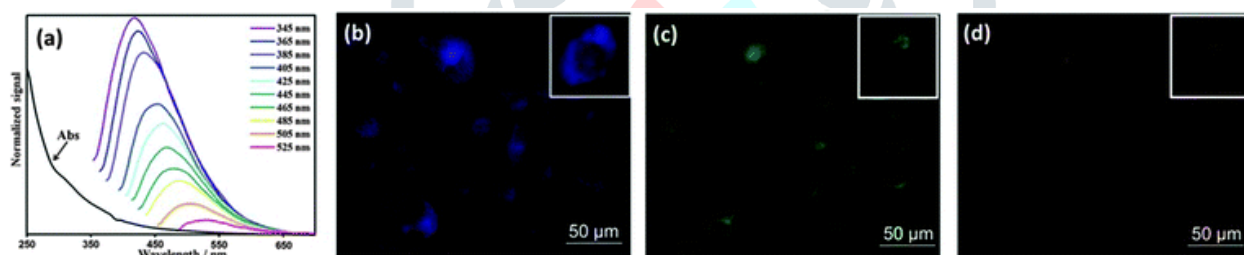


Fig 4 a) Emission spectra of CQDs at different excitation wavelengths; fluorescence images of MCF-10A cells treated with CQDs upon excitation with (b) UV, (c) blue and (d) green light.

Huang et al. investigated (Fig 5) the effect of the injection route on the distribution, clearance and tumor uptake of CQDs. It was learnt that CQDs are quickly and effectively excreted from the body when intravenous, intramuscular and subcutaneous injection routes are used. Additionally, the high tumour-to-background fluorescence contrast and low fluorescence levels in other tissues and organs demonstrated the suitability of CQDs to act as photosensitizers as they are able to localize selectively into tumours [43]. Besides serving as drug carriers and fluorescent tracers, CQDs were found to be able to control drug release.

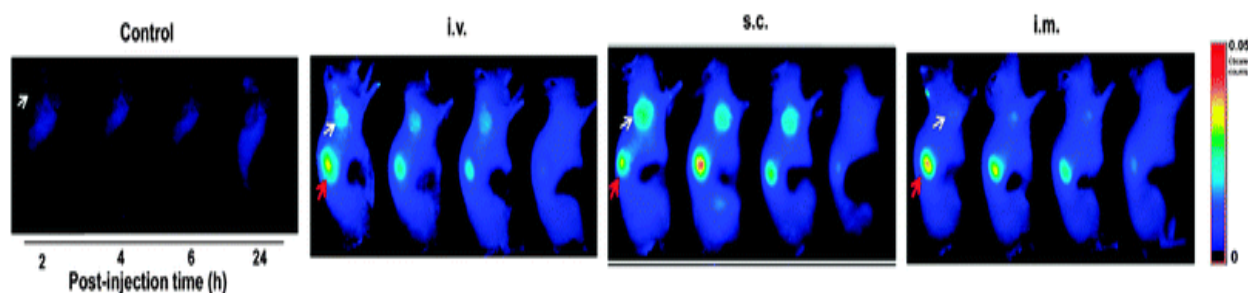


Fig 5 Fluorescence images of tumour-bearing mice

4.3. Photo catalysis

In recent years, photo catalytic process has gained tremendous interest as greener outlook for organic synthesis. Photo catalysis has been a source of motivation for Researchers that sunlight is effectively an inexhaustible energy source. However, the high energy of UV and short wavelength visible light may harmfully for the organic compounds. The demonstrated capability of harnessing long wavelength light and energy exchange with solution species of CDs offers an excellent opportunity for the application as photo catalysts in organic synthesis [38]. To prove the versatility of the nanocomposite photocatalyst, Liu et al. reported the utilisation of the photochemical properties of AuNP–CQD nanocomposite for high-efficiency and high-selectivity photo catalytic systems for green oxidation of cyclohexane. The AuNP–CQD nanocomposites yielded 63.8% conversion efficiency and 99.9% selectivity for the oxidation of cyclohexane to cyclohexanone using H_2O_2 as the oxidant under visible light at room temperature. This approach gains more attention since it provides an exciting solution for the development of high-performance carbon dots based photo catalyst and green synthetic routes for the chemical industry [44]

H. T. Li et al. have synthesized a water-soluble fluorescent carbon quantum dot and proved as photo catalyst. They have engineered the band gap of the photo catalyst to enhance the performance of TiO_2 . They have taken methylene blue (MB) as a model compound and proved that TiO_2 –CQD nanocomposite are able to completely degrade MB (50 mg/mL) within 25 min under visible light irradiation, where only <5% of MB is degraded when pure TiO_2 is used as the photo catalyst [45].

Zhang and co-workers have succeeded in utilising TiO_2 –CQD nanocomposite as photo catalyst to generate H_2 through water splitting. They observed that TiO_2 nanotubes arrays loaded with CQDs are capable of producing H_2 from water through photo catalysis under visible light [46]. In addition to being used as photo catalysts, CQDs have been capturing the attention of researchers as potential photosensitizers in solar cells. It is likely that this kind of CQD composites will offer new opportunities in various applications

5. Conclusion

In summary, we have described the various synthetic methods, properties, and applications of natural carbon dots (CDs). The physicochemical properties of CDs, including their fluorescence properties without photo-bleaching and photo blinking, their facile emission tuning and their chemical stability, enable the development of highly sensitive sensing platforms. It is believed that CDs will play an increasing role in analytical and bio analytical science in the near future. Major applications are bioimaging and use in solar cells, sensors, and catalysis. Although much research effort has been committed to developing latest natural resources, new synthetic methods, new applications, and materials and devices with improved performance, some challenges still stay behind.

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