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Review

A Review on the Use of Biochar Derived Carbon Quantum Dots Production for Sensing Applications

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Abstract: Since their discovery, carbon dots have attracted a great deal of interest for their perspective biological applications. Nevertheless, the quenching of carbon dots photoluminescence represents an interesting feature for quantitative analysis in very low concentration of many species. A particular approach for the production of carbon dots is the use of biochar, a carbonized biomass, as a precursor. In this work, we overview the main achievements accomplished by using biochar-derived carbon dots for detecting and quantifying inorganic and organic species. We also provide background knowledge of the main properties, production and purification routes of carbon dots.

Keywords: biochar; carbon quantum dots; chemical sensing



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1. Introduction

Biochar (BC) is a carbon material recovered from the conversion of biomasses under high temperature in a poorly or non-oxidative atmosphere [1]. BC is commonly used in environmental remediation [2] and as soil amelioration [3]. Nevertheless, BC has yet to experience a real breakthrough. Maroušek et al. [4] sharply pointed out the failure of BC use in land carbon sequestrations, as the high cost prevents massive use of BC as an agricultural amendment. This unneglectable issue becomes marginal if BC is used for high cost applications such as energy storage [5,6], as a flame retardant additive [7–9], a conductive filler for improving mechanical and electrical properties of both a polymeric [10–17] and cement matrix [18–21], and as a catalyst [22].

Nowadays, BC has been considered in many fields, but there is still a search for so-called “killer applications” that will make it the carbon material for a sustainable world.

A good chance is represented by the conversion of pristine BC into nanostructured materials with superior electric performances. For this purpose, Carbon Dots (CDs) have gained great attention as the newest carbon-based nanomaterials.

CDs are a class of fluorescent carbon-based nanomaterials discovered by chance in 2004, when Xu et al. [23] tried to purify single-walled carbon nanotubes. CDs have been shown to be a valid alternative to Quantum Dots (QDs) thanks to their simple preparation methods and multiple inherent properties such as intrinsic biocompatibility, water solubility, chemical inertness, and photoluminescence [24]. This wide spectrum of properties allows them to be used both in diagnostic and therapeutic fields, for example as a vehicle for drug release, as probe molecules (thanks to their excellent fluorescence properties), or for bioimaging and biosensing techniques [25–27].

Over the years, many hypotheses have been made about CD structure [28]. Of note, CDs are very different according to the various precursors used and preparation routes

followed. Nevertheless, several authors have proposed a general model for CDs with an inner graphitic core with amorphous region close to the edges [29]. Others have suggested interpretative models based on an amorphous core [30]. The more reliable classification based on the structure was reported by Mintz et al. [31], who classified three great families of CDs: (i) graphitic, (ii) nitride based, and (iii) polymeric ones. Each group displayed peculiar characteristics and chemical signatures. Graphitic CDs have attracted the greatest interest due to their tremendous versatility and similarity to graphene derivatives. Graphene CDs have proved to be a very powerful species for chemical sensing and bioimaging [32,33].

However, the synthesis of these nanomaterials requires considerable energy consumption and a chemical oxidation step which is performed in environmental unfriendly conditions [34]. Accordingly, research has investigated new productive routes based on environmentally sustainable materials for the production of high performance CDs for sensing uses.

In this review, we try to provide an overview, updated at the end of 2021, of the research concerning the use of BC for the production of CDs and of their applications in chemical sensing, providing a comprehensive overview of inorganic and organic species detection.

2. Carbonization of Biomass: From BC to BCCDs

2.1. BC Production

As stated above, BC is produced through thermochemical cracking of biomasses under different conditions. The main routes for biochar production are torrefaction, hydrothermal liquefaction, pyrolysis, and gasification. The main and more relevant difference between these routes is represented by the different temperature and reaction medium used.

During torrefaction, process temperature can reach up to 200–350 °C, achieving only a partial carbonization of biomass [35]. BC produced from biomass torrefaction displays a carbon content of up to around 50 wt.% with yields of up to 70% [36], but can reach values close to 80 wt.% through the use of microwave assisted processes [37–41].

Under pyrolytic conditions, process temperature is increased above 400 °C, promoting advanced cracking reactions in an oxygen-free atmosphere with yields of BC ranging from 30 wt.% up to 50 wt.% [42].

Contrary to pyrolysis, gasification occurs in an oxidant atmosphere such as air [43], oxygen, or steam [44] at temperatures higher than 800 °C with or without the addition of a catalyst [45]. The main gasification output is represented by gas, but BC is also produced in a low amount and with high ash content [46].

Hydrothermal liquefaction (HTC) is a different route compared to the previous ones because it is run in a water medium at low temperatures ranging from 140 °C up to 380 °C under pressure in the range of 4 atm up to 220 atm [47]. The hydrothermal liquefaction process is far less efficient than the other for BC production, with maximum yields of up to around 15 wt.%. Nevertheless, BC produced using this last approach shows a very high surface area and a great amount of polar functionalities on its surface [48].

2.2. BCCDs Production

BCCDs production converts low-value biomass waste into valuable and useful materials. There are essentially two main methodologies for the synthesis of BCCDs: top-down and bottom-up methods. Top-down methods involve the cleavage of bigger carbon structures while bottom-up methods build up the structures from small precursors. Common methods for BCCDs production include HTC, microwave-hydrothermal, pyrolysis carbonization, etc.

HTC exploits temperature (180–380 °C) and pressure for a few hours to convert BC in BCCDs for a wide variety of applications [49]. Microwave-hydrothermal method uses microwaves to heat water, an approach not commonly used, yet it allows for obtaining narrow and uniform size distribution (generally between 1 and 5 nm) [50]. Pyrolysis is one of the common methods for BCCDs production and involves the decomposition of

a carbon source by heat. Also, in this case, the as-prepared BCCDs show a narrow size distribution ranging from 0.4 to 2.0 nm [51].

There are many studies that describe BCCDs production exploiting simple heating of organic molecules such as urea, aromatic amine, or organic acids [52]. This approach involves different stages, including dehydration, polymerization carbonization, and passivation [53].

Many authors have observed that higher reaction temperatures influence particle size and QY value. In particular, the higher the reaction temperature (up to 180 °C under hydrothermal conditions), the lower the particle size (down to 3 nm) [54].

The unique combination of spectroscopic and morphological features of carbon dots, as shown in Figure 1 according Mintz [31], represent the most characteristic properties of CDs.

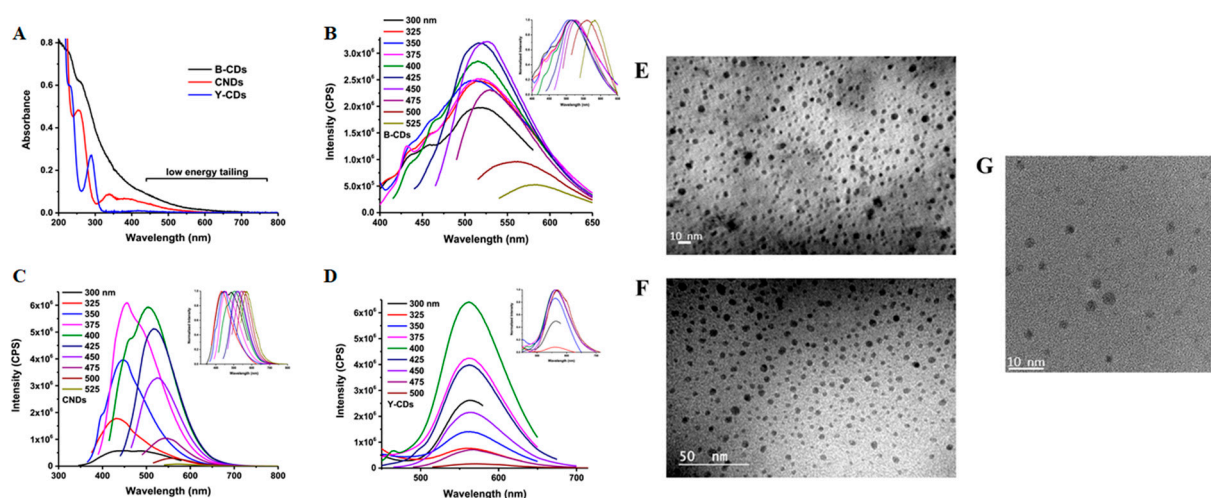


Figure 1. UV-Vis (A), fluorescence (B–D) and TEM (E–G) of three CDs produced from carbon soot (B-CDs), from citric acid and urea (CNDs), and from citric acid and 1,2-diaminebenzene as reported by Mintz [31]. Reprint with all permissions from Elsevier.

Other studies have shown how a low-temperature carbonization and simple filtration can be used to synthesize BCCDs. The as-prepared CDs exhibited small particle sizes (down to 2 nm) and good stability in a wide range of pH values (2–11) [55].

As stated, HTC is the preferred thermochemical route for the production of BCCDs, but is not sufficient to produce pure materials. A key step for the recovery of BCCDs is the purification of BC precursor through dialysis, as shown in Figure 2.

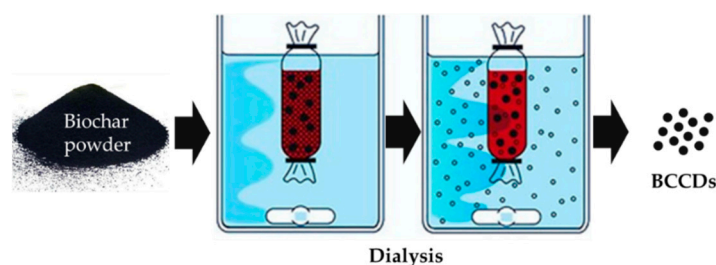


Figure 2. Dialysis purification of BC for the isolation of BCCDs.

Dialysis purification of suspended BC allows for cutting out particles of different molecular size, isolating them inside or outside the membrane. Dialytic procedure is the unavoidable stage for any CDs production, and could be coupled with other approaches such as a chromatographic one for further refining of the CDs size distribution [56,57].

Size distribution is strongly related to all the CDs features such as PL [58] and biological exploits [59].

3. BCCDs for Sensing Applications

3.1. BCCDs Properties

CDs are carbon based nanomaterials with an average size of down to few nanometers regrouped in three main families: graphene-like, carbon nitride, and polymeric CDs [60].

The most relevant property of CDs is undoubtedly the photoluminescence (PL). PL of CDs is a complex phenomenon involving at least four different mechanisms [61]. The first is the quantum confinement effect due to the conjugated π -domains, which is related to the inner core structure of CDs [62]. The second effect is related to the put shell of CDs and is due to the hybridization of the carbon atoms backbones and to the residual functionalities [63]. The third one is the simplest and is due to fluorescent molecules entrapped and bonded to the CDs structures. The last one is the crosslink enhanced emission and it is characteristic of polymeric CDs [64].

Similar to graphene CDs, BCCDs exploit the first two mechanism mentioned due to their high carbon content. Yu et al. [65] comprehensively described the PL of graphene-like CDs by varying the core/shell ratio and surface functionality, hypothesizing an emission mechanism, as shown in Figure 3.

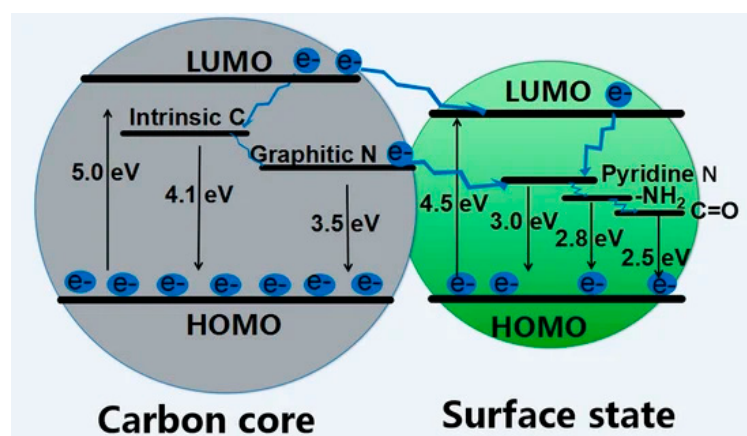


Figure 3. Scheme of the luminescence pathway and corresponding energy in graphene CDs with different core/shell ratio and surface functionalities. Reprinted with permission from [65] under CC BY 4.0.

PL is also the key for using CDs for chemical sensing due to the quenching phenomena occurring in the presence of metal ions [66,67]. Furthermore, the interaction between CDs and organic molecules could also alter PL emission [68].

The mechanisms laying behind PL quenching are numerous (static quenching [69], dynamic quenching [70], Förster resonance energy transfer [71], photoinduced electron transfer [72], surface energy transfer [73], Dexter energy transfer [74], inner filter effect [75]), and they are related to the interaction occurring between CDs and the quencher.

Static quenching is due to the formation of a ground state complex between CDs and a quenching agent, while the dynamic one occurs as a consequence of the diffusion process of a quenching agent while CDs is in its excited state [76].

Förster resonance energy transfer takes place between a quenching agent and CDs over great distances up to 10 nm, interacting mainly through dipole-dipole interaction [77]. Contrarily, a short scale interaction length is necessary for photoinduced electron transfer occurring with the association of CDs and a quenching agent on a sub-nanometric scale [78]. Surface energy transfer is more related to the quenching of inorganic dots as a consequence of the interaction of surface plasmons and a fluorophore [79], but could also occur during interactions between CDs and small metal clusters [80]. Dexter energy transfer takes place on the same scale length of Förster resonance energy transfer, but involves an orbital overlapping [81]. The inner filter effect has been considered an error in PL measurements,

but is a real phenomenon due to the overlap of the absorption spectrum of the quencher with the excitation or emission spectrum of CDs [82].

PL emission modification caused by external stimuli represent the pillar of use of CDs for a sensing application, as we discuss in the next sections.

Nevertheless, CDs derived from highly graphitic precursors could be also be used for electrochemical sensing [83].

3.2. BCCDs for Detection of Inorganic Species

Several studies have been devoted to the use of many BCs for the detection of metal ions [84]. Nevertheless, BCCDs represent a new approach in the field with unravelled potentialities, as summarized in Table 1.

Table 1. Summary of the main study on inorganic ions in water phase detection by using BCCDs materials.

Application	Production Route	Average Size (nm)	Quantum Yield (%)	Detection Limit (μM)	Linearity Range (μM)	Ref.
Fe(III) detection	• Hydrothermal conversion (180 °C) of domestic waste	15.3	28	0.0001	0.001–0.01	[85]
	• Hydrothermal conversion (160 °C) of wheat, rice and corn straw	2.5	3.5	5	5–500	[86]
	• Pyrolysis up to 400 °C of mango peel and oxidation with sulfuric acid	3.7	11.5	Not reported	4–200	[87]
	• Hydrothermal conversion (180 °C) of sweet potato and glycine	3.5	2.8	0.3	1–100	[88]
	• Hydrothermal conversion (200 °C) of orange peel, ginkgo biloba leaves, paulownia leaves and magnolia flower	2.6	8.1	0.08	0.2–100	[89]
	• Hydrothermal conversion (200 °C) of Lycii Fructus	3.3	17.2	0.02	1–30	[90]
	• Hydrothermal conversion (200 °C) of lignin	4.9	23.7	0.8	1–300	[91]
	• Hydrothermal conversion (200 °C) of waste rice and glycine	2.7	23.5	0.8	30–200	[92]
	• Hydrothermal conversion (150 °C) of wood waste	<10	28.3	32	150–500	[93]
	• Hydrothermal conversion (180 °C) of fruit extract	5	8.7	70	125–500	[94]
• Hydrothermal conversion (180 °C) of blue grass	8.5	7.3	1	5–25	[95]	

Table 1. Cont.

Application	Production Route	Average Size (nm)	Quantum Yield (%)	Detection Limit (μM)	Linearity Range (μM)	Ref.
Cu(II) detection	• Hydrothermal conversion (200 °C) of bamboo leaves and amines	3.6	7	0.1	1–140	[96]
	• Microwave carbonization of mushroom 800 W	2.6	7.6	0.004	0.01–500	[97]
	• Microwave carbonization of fruit bunch 800 W			0.4	1–400	[98]
	• Peroxidation and hydrothermal conversion (200 °C) of prawn shells	7.6	12.3	0.005	0.010–1.1	[99]
Al(III) detection	• Hydrothermal conversion (160 °C) of <i>Pyrus pyrifolia</i>	2	10.8	0.003	0.005–100	[100]
	• Hydrothermal conversion (180 °C) of algae	68	10.2	<0.001	0.2–70	[101]
CrO ₄ ²⁻ detection	• In-flow hydrothermal conversion (450 °C) of glucose	4.5	0.3	0.002	1–500	[102]
Hg(II) detection	• Microwave carbonization of lotus root using 800 W	9.4	5.2	0.019	0.2–60	[103]
	• Hydrothermal conversion (200 °C) of orange juice and amines	3	31.7	Not reported	4–32	[104]
	• Hydrothermal conversion (160 °C) of Pineapple Leaf Fiber	4.6	Not reported	<0.001	0.2–60	[105]
	• Low temperature pyrolysis (300 °C) of pigeon feathers, egg and manure	4.2	33.5	0.001	0.12–1.66	[106]
Ag(I) detection	• Long time hydrothermal conversion (180 °C, 8 days) of bean pod and onion	6	7.6	0.037	0.1–25	[107]
	• Hydrothermal conversion (260 °C) of purple perilla	2.8	9	0.001	0.002–0.010	[108]
AsO ₄ ³⁻ / AsO ₃ ³⁻ detection	• Microwave carbonization of quince fruit using 800 W	4.9	8.6	0.02	0.2–2	[109]
Co(II) detection	• Microwave carbonization of kelp and mines using 800 W	3.7	23.5	0.4	1–200	[110]
Cs(I) detection	• Hydrothermal conversion (190 °C) of maple leaves	10	Not reported	0.02	0.1–100	[111]

Table 1. Cont.

Application	Production Route	Average Size (nm)	Quantum Yield (%)	Detection Limit (μM)	Linearity Range (μM)	Ref.
ClO^- detection	Hydrothermal conversion (180 °C) of pepper	7	7.1	0.05	variable	[112]
S^{2-} detection	Hydrothermal conversion (200 °C) of carrots	4.8	Not reported	0.06	0.1–8	[113]
F^- detection	Ultrasound carbonization of sugarcane bagasse	12	27	Not reported	10–160	[114]

Evaluation of Fe(III) and Fe(II) is a key issue in any water stream due to the large use of iron salt as a flocculant agent in wastewater treatment facilities [115].

Das et al. [85] converted several waste biomass (rose petals, banana peel, coffee, and tea waste) through the hydrothermal process at 180 °C, producing green emitting BCCDs. Authors reported wide size distribution based on the different precursors used from 7.2 nm using rose petals of up to 15.3 nm using spent coffee grounds. Through an optical approach, authors reported a range of quantification of Fe (III) in water from 1 nM up to 100 nM. Similar results were achieved for the detection of Cr (VI) ions. Interestingly, authors described an on-off behavior of the BCCDs after the addition of the metal ions solution, as reported in Figure 4.

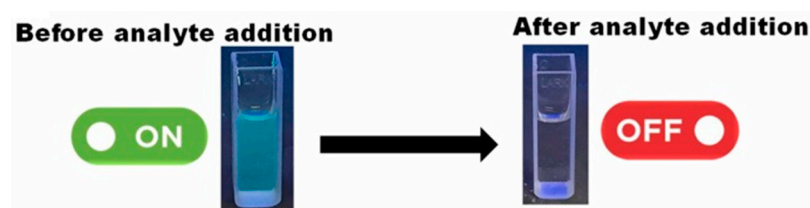


Figure 4. Fluorescence quenching of blue emitting BCCDs in the presence of Fe(III) ions reported in [85]. Reprinted with permission from Elsevier.

Very similar behavior was observed for low temperature produced BCCDs reported by Şenol et al. [116]. Authors suggested that the on-off behavior was due to the formation of a non-radiative complex between Fe(III) and surface groups of BCCDs. Furthermore, authors observed the same trends in the presence of strong oxidant agents such as hypochlorite ions able to oxidize the hydroxyl functionalities. Accordingly, they concluded that the presence of hydroxyl residues represent a must-have condition for iron sensing.

Ding and co-workers [86] used wheat, corn, and rice straw for the realization of blue emitting BCCDs with an optimal excitation wavelength in the range from 350 nm up to 390 nm. Authors pointed out that the emission was due to the transitions $\pi^* \rightarrow \pi$ of C=C and $\pi^* \rightarrow n$ of C=O. The sensitivity of the BCCDs was not so high, but still interestingly reached a detection limit of up to 5.23 μM for Fe(III) in a watery solution. Similar results were reported by Jiao et al. [87] by using mango peel as a BC precursor. Authors used pyrolytic conditions (400 °C of processing temperature in a nitrogen atmosphere), together with an oxidative process with sulfuric acid producing BCCDs with an average size in a range of 2 nm up to 6 nm and a quantum yield of $8.5 \pm 0.2\%$. BCCDs emission was stable both in acidic and basic environment media, reaching a detection limit of Fe(III) up to 5 μM . Improved results on Fe ions detection were achieved by Shen et al. [88] using sweet potato under hydrothermal conditions for the production of hydroxyl rich BCCDs with a maximum emission at 440 nm. Authors claimed a limit of detection for Fe(III) up to 0.3 μM .

Wang et al. [89] produced well-performing BCCDs using various exotic biomass with high water solubility and stability in wide pH and temperature ranges. The PL quenching

induced by the presence of Fe(III) led to a very low limit of detection of up to 0.08 μM . Similar results were achieved by using *Lycii Fructus* [90] and lignin [91].

Varying the BC precursor is not the only way to improve the iron detection performance of BCCDs. A very effective way to produce more performing materials is represented by heteroatom doping.

Qi et al. [92] produced nitrogen doped BCCDs using rice waste and glycine, achieving materials with a quantum yield of up to 24% and a maximum emission of up to 440 nm. Authors reported a low Fe(III) detection limit of up to 0.7 μM . Ahn et al. [93] produced BCCDs with blue emission and a quantum yield of 23%. Blue emitting BCCDs showed a higher detection limit of up to 32 μM but they were able to detect Fe(III) also in in vivo systems. Atchudan et al. [94] converted *Chionanthus retusus* fruit extract using a hydrothermal carbonization method operating at 180 $^{\circ}\text{C}$ for 6 h. The nitrogen-rich precursor led to the formation of nitrogen doped BCCDs with amine, pyridine, and pyrrole functions on the shell and an average size of up to 5 nm with an interlayer distance of 0.21 nm. Authors demonstrated a highly durable fluorescence with a quantum yield of 9% for the as-synthesized materials and a detection limit of 70 μM in vivo for Fe(III) detection.

Krishnaiah et al. [95] converted blue grass through hydrothermal routes at 180 $^{\circ}\text{C}$ for 36 h, producing nitrogen doped BCCDs. Authors observed fluorescence with a significant redshift from 370 to 470 nm using wavelengths ranging from 280 up to 400 nm, as shown in Figure 5.

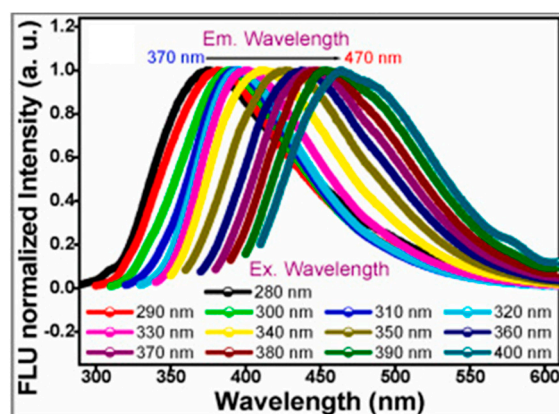


Figure 5. Red shift of green emitting BCCDs as reported in [95]. Reprinted with all permissions from Elsevier.

Excitation dependent emission represents a crucial issue in the understanding of CDs emission and is debated by several authors [117,118]. Authors suggest that this phenomenon was due to $n \rightarrow \pi^*$ transition occurring through non-bonding electrons of carbonyl and carboxylic groups of BCCDs outer shell. This behavior was in agreement with a structural study reported by Mintz et al. [31] and was reasonably affected by nitrogen atom inclusion. Authors also reported a quite low quantum yield of up to 7% and a high hydrophilicity, allowing the detection of both Fe(III) and Mn(III) ions in water medium. Authors reached a detection limit of up to 1.4 μM and a linearity range from 5 up to 25 μM . Furthermore, authors proved the stability of BCCDs in water solution evaluating the emission spectra of BCCDs in a 100-day period without observing any appreciable change. Nevertheless, these materials showed an appreciable loss of selectivity in the presence of Cd(III) and Pb(III).

Detection of Cu(III) is also a relevant task for water and biological applications due to the harmful potential for marine ecosystems [119,120] and the human body [121].

BCCDs are solid solutions to evaluate the copper cations concentration in watery medium due to the strong PL quenching induced by the Cu(III).

Liu et al. [96] produced a blue emitting BCCDs through the conversion of bamboo leaves and diamines at 200 $^{\circ}\text{C}$ for 6 h. The resulting BCCDs showed a maximum emission at

450 nm and a very low detection limit for Cu(III) in water media up to 115 nM. Furthermore, authors reported a remarkably selective quenching induced by Cu(III) over other metals (i.e., Co(III), Ca(III), Ni(III), Mn(III), Hg(III), Pb(III), Ba(III), and Cd(III)) while cations such as Fe(III) and Hg(III) appreciably interfered.

Bhamore et al. [97] used a microwave-assisted carbonization procedure for the conversion of seeds into 2.5 nm sized BCCDs. Authors used a monomodal microwave oven with a power of up to 800 W for 2 min and isolated the purified BCCDs through dialytic methods. The resulting BCCDs acted as “turn-off” sensors with an emission maximum at 468 for Cu(III) reaching a limit of detection of 4.3 nM. Furthermore, authors did not observe PL quenching in the presence of other metal cations, suggesting the production of a highly selective probe for Cu(III). Kamarol Zaman et al. [98] also produced blue emitting BCCDs using microwave-assisted route and empty fruit bunch. BCCDs produced showed an emission peak at around 420 nm under UV irradiation. Authors reported a good detection limit for Cu(III) of up to 0.42 μ M.

Gedda et al. [99] pre-oxidized prawn shells and hydrothermally converted them into blue emitted BCCDs with an average diameter of up to 4 nm and emission peaked at 390 nm under UV irradiation. As shown in Figure 6, the selectivity of these species for Cu(III) was also quite good in real marine water samples.

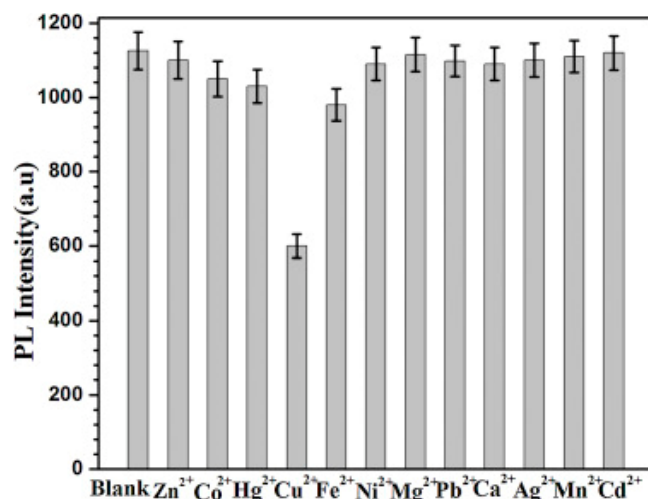


Figure 6. PL quenching reported by Gedda et al. [99] in presence of different metal ions with a concentration of up to 5 μ M. Picture reprinted with all permissions from Elsevier.

Authors suggested that the selectivity observed was due to the specific quenching mechanism related to the interaction between Cu(III) and amine residue with the formation of cupric amine acting specific UV/visible absorption.

Aluminum ions are another species that could represent a serious threat to human health [122]. Accordingly, Al(III) monitoring is also very relevant, and the use of low detection limit analytical routes is of great interest.

Accordingly, Bhamore and co-workers [100] developed an analytical route for Al(III) detection by using BCCDs produced from the hydrothermal conversion of waste pears. The blue emitting BCCDs showed a peak of emission close to 470 nm under UV irradiation and a size of up to around 2 nm. Authors reported a very low detection limit of 2.5 nM and a great selectivity to Al(III) in the presence of cations, anions, and organic species. This was justified by the selective formation of stable Al(III) chelated species on the outer shell of BCCDs that induced an irreversible quenching of PL. Similarly, Rao et al. [101] synthesized a dual emission BCCDs through the conversion of several algae under hydrothermal conditions at 180 °C for 10 h. The produced BCCDs showed two emissions peaked at 470 nm and 670 nm under a single excitation. Interestingly, the emission at 470 nm was selectively quenched by Al(III) even in the presence of other ions, while the one at 670 nm

was quenched by water. These BCCDs have been proposed as reliable chemosensors for both Al(III) and water evaluation in commercial fruit juices.

Baragau et al. [102] faced the issue of Cr(VI) detection by using BCCDs. Authors proposed an innovative in-flow hydrothermal route operating at 450 °C and with a constant pressure of up to 24.8 MP. BCCDs produced displayed a size of up to 2.3 nm, with an emission peaking at 446 nm on excitation at 360 nm. Authors claimed a limit of detection for Cr (VI) of up to 2 µM. Authors also reported the possibility of using the same BCCDs for Fe(III), but they did not evaluate the competition between the two inorganic species.

Another metal cation detectable by using PL quenching of BCCDs is Hg(III). Hg(III) is among the most toxic metal ions, having dramatic effects on human health [123]. Accordingly, Gu et al. [103] developed BCCDs from microwave carbonization of lotus root for detection of Hg(III) in water. The BCCDs synthesized showed a high content of nitrogen up to around 5% and a diameter close to 10 nm. Nevertheless, they were able to not only detect Hg(III) with a detection limit of 17 nM, but also to selectively capture the mercury ions without releasing them. These properties also allowed BCCDs to be used for environmental remediation purposes. Nitrogen doping is an essential feature for Hg(III) sensing through BCCDs, as proved by many authors [104,105]. The abundance of nitrogen is directly related to the presence of amine and pyridine residues that boosted the capture of Hg(III) with an enhancement of PL quenching. The most effective BCCDs doping is represented by the simultaneous insertion of nitrogen and sulfur atoms, as mentioned by Ye et al. [106]. Authors co-pyrolysed pigeon feathers, egg, and manure and purified BCCDs through dialysis. The recovered materials showed a blue emission centered at 475 nm and an average size of up to 4 nm. The presence of sulfur atoms mainly included in the graphitic structures promoted the formation of stable bonds with Hg(III), reaching a detection limit of up to 10 nM.

The very same approach was used by Lu et al. [107] by hydrothermal treating bean pod and onion for 8 days at 180 °C for the detection of Ag(I). The blue emitting BCCDs reached a limit of detection of 37 nM, showing the best nitrogen/sulfur ratio to be close to 3. Even better results were achieved by Zhao et al. [108]. Authors hydrothermally treated purple perilla at 260 °C after sonication in water medium, producing BCCDs with the astonishing detection limit of Ag(I) up to 1.4 nM. Similar results were achieved in the detection of As(III) [109] and Co(III) [110] by using microwave-assisted synthetic strategies.

Interestingly, Boruah et al. [114] reported an ultrasound-induced carbonization of biomass for the production of BCCDs able to detect fluoride ions. Authors converted sugar cane bagasse into blue emitting BCCDs that after doping with Eu(III) could be used for detecting fluoride down to a concentration of 10 µM.

Chellasamy et al. [111] converted maple leaves by using hydrothermal treatment at 190 °C for 8 h producing blue emitting BCCDs. Authors reported the formation of small BCCDs with an average size of up to 1–2 nm with a carbon structure quite ordered, as proved by the analysis of Raman spectra. Authors used the prepared materials for cesium detection in water media achieving a linearity range from 0.1 up to 100 µM and a detection limit of up to 0.16 µM without observing any appreciable interference effects from other ions. Interestingly, authors observed an appreciable modification of Raman spectra.

Yin et al. [112] developed BCCDs with symmetric emission spectra, large Stokes shifts, improved resistance to photobleaching, and excitation dependent emission. Curiously, authors reported a two-emission spectra with one emission peak centered at around 280 nm under UV irradiation and another one in the range from 450 nm up to 600 nm under visible light. They suggest that this behavior was due to two different mechanisms; one due to $n \rightarrow \pi^*$ active in UV region and the other due to several structural factors (i.e., particle sizes distribution, different emissive centers, multiphoton processes). These two emission phenomena led to two linear ranges, one from 0.1 up to 10 µM, and one from 10 up to 300 µM. Authors achieved a very promising result in hypochlorite detection in real water samples with percentage errors of around 2%.

Jin et al. [113] produced BCCDs conjugated with polyethyleneimine and Nile Blue for direct sensing of sulfide anions. Authors realized the chemical probe by assembling the

additive and BCCDs through supramolecular electrostatic interactions. Authors quenched the emission of BCCDs via inner filter effect by adding Cu(III) and using the non-emitting BCCDs adduct for the detection of sulfide. Sulfide species were able to tightly bond with copper ions and were removed from BCCDs, increasing the emission. Accordingly, this was one of the first studies reporting an off-to-on behavior of BCCDs in sensing applications. Authors reached the interesting detection limit of 0.06 μM with a linearity range from 0.1 up to 8.0 μM .

Other BCCDs systems were able to detect more than one heavy metal but not simultaneously [95,124] due to the coordination of metals on their outer shell.

Nevertheless, BCCDs uses are not limited to the detection of a single species, but could be used to assemble chemical platforms able to simultaneously detect multiple species. As reported by Fu and co-workers [125], waste animal bones could be converted through hydrothermal processes into BCCDs. These materials have been used to build a multi-channel array able to quantify and discriminate up to five different metal ions by modulating the PL emission. Authors claimed an accuracy up to 100% for individual, binary and ternary mixture of Ag (I), Cu(III), Hg(III), Fe(III) and Pb(III). Similarly, Plácido et al. [126] converted microalgae BC into BCCs producing a transducer for detecting Pb(III), Cu(III), Cd(III), and Ni(III) with good stability under a wide range of pH and resistant to photo-bleaching. Authors reported good detection limits ranging from 12 nM to 2 mM with an enhancement of detectability using slightly basic pH.

3.3. BCCDs for Detection of Organic Species

PL quenching of BCCDs is not limited to the interaction with inorganic species, but could also be induced by probe molecules [127], as summarized in Table 2.

Table 2. Summary of the main study on organic detection by using BCCDs materials.

Applications	Production Route	Size (nm)	Quantum Yield (%)	Detection Limit (μM)	Linearity Range (μM)	Ref.
Sensing of prilocaine	• Hydrothermal conversion (200 °C) of saffron	7.5	23.6	1.8	0.003–0.400	[128]
Sensing of dimethoate	• Pyrolysis (700 °C) of food waste	4.2	Not reported	0.06	0.15–5	[129]
Sensing of imatinib	• Hydrothermal conversion (180 °C) of starch	Not reported	Not reported	0.002	10–400	[130]
Sensing of glyphosate	• Hydrothermal conversion (200 °C) of wool	2.8	16.3	0.012	0.025–25	[131]
Sensing of biothiols	• Hydrothermal conversion (200 °C) of silkworms' excrements	62	13.1	0.2	1–1000	[132]
Sensing of ascorbic acid	• Hydrothermal conversion (180 °C) of milk powder in the presence of FeCl_3	2.9	8.7	9	20–500	[133]
Sensing phoxim	• Hydrothermal conversion (180 °C) of Lycii Fructus			0.04	0.1–100	[134]
Sensing of baicalin	• Low temperature carbonization (200 °C) of grape peels mixed with urea	7	Not reported	0.04	0.1–20	[135]

Table 2. Cont.

Applications	Production Route	Size (nm)	Quantum Yield (%)	Detection Limit (μM)	Linearity Range (μM)	Ref.
Sensing of tetracyclines	Hydrothermal conversion (200 °C) of waste tobacco	6.3	13.7	0.05	1–120	[136]
	Hydrothermal conversion (200 °C) of sweet potato peel	31	8.9	0.015	0.025–1	[137]
	Hydrothermal conversion (200 °C) of waste rice	2.7	23.5	0.24	1–250	[92]
	Hydrothermal conversion (200 °C) of tobacco	2.1	27.9	0.01	0.04–6	[138]
	Hydrothermal conversion (200 °C) of carp roe	7.6	13.4	0.04	0.1–50	[139]

Ensafi et al. [128] synthesized BCCDs from saffron by hydrothermal treatment for sensing of prilocaine. BCCDs showed a quantum yield of up to 24 and a size lower than 10 nm with an emission peaking at 460 nm. Authors reported a very interesting detection limit of prilocaine in water medium of up to 1.8 nM that was better than results achievable with LC-MS and comparable with GC-MS–electron impact ionization selected ion monitoring techniques. Furthermore, BCCDs were highly selective in real blood medium, as shown in Figure 7.

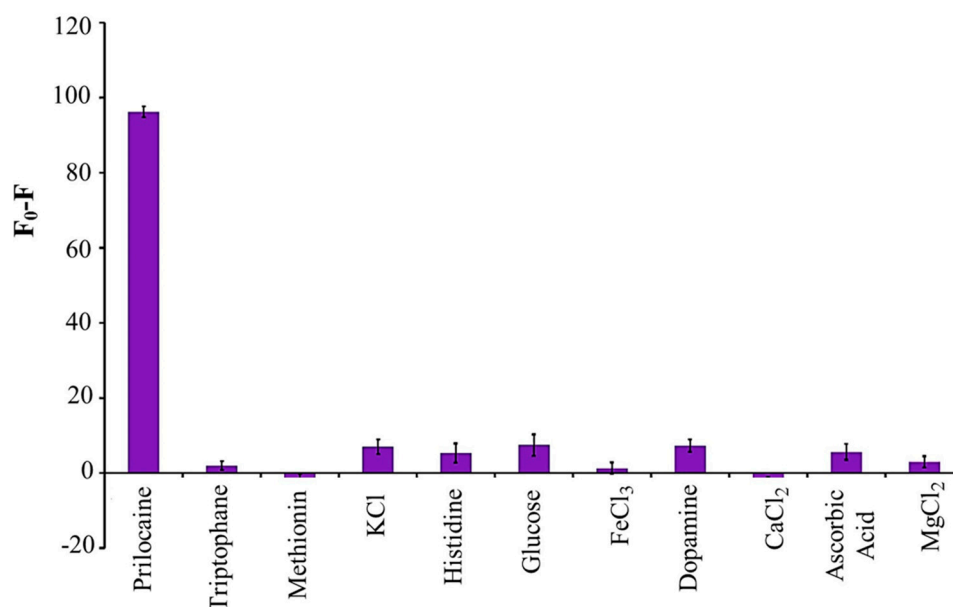


Figure 7. Selectivity calculated as differences between neat and conjugated of the BCCDs reported in [128] for prilocaine in real human blood at pH 4. Picture reprinted with all permissions from Elsevier.

Liu et al. [129] pyrolyzed pork ribs at 700 °C, producing BCCDs of 3–4 nm size with an emission peaked at 453. Authors used BCCDs for detection of dimethoate, finding a detection limit of 64 nM at pH 11 in water medium. A similar strategy was used by Yan et al. [130] for the detection of imatinib. Authors reached a detection limit of up to 2 nM as a consequence of a strong charge transfer quenching phenomenon. Wang et al. [131] hydrothermally converted waste wool at 200 °C, producing BCCDs with a 480 nm emis-

sion under UV irradiation. Authors combined this material with silver nanoparticles for glyphosate detection in water medium, reaching a detection limit of up to 12 nM.

Lu et al. [132] approached the sensing of biothiols by synthesizing BCCDs from excrements of silk worms and quenched their fluorescence emission by adding Fe(III). The non-emitting BCCDs were able to detect the presence of thiols containing species due to the ability of the iron sites to form stable complex bonding thiols functions. This behavior was detrimental for quenching phenomena and allowed for detecting cysteine and glutathione with detection limits close to 4 μM .

Tang et al. [135] carbonized grape peels mixed with urea at a low temperature (200 °C) to produce highly nitrogen-doped BCCDs for flavonoid detection. Their simple solid approach paved the way to easily-scalable nitrogen doped BCCDs production able to achieve detection limits approaching 0.05 μM .

Fan et al. [133] used a very close approach to detect ascorbic acid. Authors directly prepared blue emitting BCCDs through the conversion of milk powder mixed with iron chloride using hydrothermal treatment. The iron-containing BCCDs were able to oxidize 3,3',5,5'-tetramethylbenzidine and quenched themselves. The quenched BCCDs were able to detect ascorbic acid to a reductive process that remove 3,3',5,5'-tetramethylbenzidine from the BCCDs, restoring the fluorescence emission and reaching a detection limit of up to 5.3 μM .

Zheng et al. [134] used BCCDs derived from Lycii Fructus mixed with silver nanoparticles for the detection of phoxim with a linearity range from 0.1–100 μM and a detection limit of up to 0.04 μM . Authors described with good detail the mechanism of detection based on complex interactions between BCCDs functions, nanoparticles, and analyte. The mechanism is based on a first interaction between silver nanoparticles and amino groups on the outer shell of BCCDs through electrostatic forces. By using a slightly acid pH, the cyano and ethoxy functions of phoxim carried positive charges and can interact with negative charges on the surface of BCCDs adducts forming a complex interactive network. This allows us to extend the detection close to the one achievable with the HPLC-MS technique.

Several studies have been focused on the detection of a particular class of antibiotics represented by tetracyclines. Tetracyclines are of paramount of importance due to their diffuse use and classification as emerging water pollutants [140].

Accordingly, Liang et al. [136] converted waste tobacco into BCCDs and used them to detect tetracyclines in water. Authors reached a detection limit of up to 1.5 μM and an accuracy for sample in the range of 30 μM to 60 μM , equal to that achieved by using HPLC quantifications.

Liu et al. [137] used sweet potato as a precursor for oxytetracycline determination with a detection limit of up to 0.013 μM that is even better than the commonly achieved one [141]. Other approaches used nitrogen doping [92] for further boosting of the BCCDs ability to detect tetracyclines in watery medium, outperforming chromatographic methods.

Miao et al. [138] converted tobacco leaves for the detection of three kinds of tetracyclines, proposing a detection mechanism based on two different effects related to surface defects and to quantum size of BCCDs. Authors produced a simple paper-based device able to visually discriminate tetracyclines from compounds such as cysteine and rose Bengal.

Furthermore, Tang et al. [139] proved the ability of BCCDs to detect tetracycline, chlortetracycline, and oxytetracycline in living cell human colon cancer cells and mouse cardiomyocytes, reaching detection limits of up to 0.05 μM . Similarly, Gunjal et al. [142] were able to detect tetracycline in urine and yeast cultivation media with a detection limit of up to 0.04 μM .

4. Challenges and Perspectives

The use of biomass for the production of CDs is very attractive due to the combination of sustainability goals and the great availability of feedstock. Nevertheless, the use of biomass reduced the synthetic tools for the researcher that is approaching BCCDs production. A common synthesis of CDs is far more tuneable [143] than one based on thermal

or hydrothermal conversion of biomass [144]. This issue could be overcome through a fine-tuning of production environment (i.e., temperature, heating rate, solvent, heating source) in order to use the biomass scaffolds to orientate the BCCDs towards nanostructure with appropriated size, functionalities, and quantum yield. Also, BCCDs represent the more solid bridge between graphene-like CDs and the other CDs families due to the tunable graphitization obtained by modifying the production process. This could represent a valuable opportunity to produce fluorescence and proper electrochemical based sensors for a great variety of analytes [145]. The field of CDs based sensing is still open for big discoveries, and anarchy is ruling the research, but we firmly hope that the advance in comprehension of CDs structure-activity will lead to more goal-oriented research in the near future.

5. Conclusions

The use of CDs as molecular probes for the detection of inorganic and organic species is becoming a topic of paramount importance. Nevertheless, interest in the use of CDs outside the biological fields has attracted the attention of environmental issues related to the CDs production routes. BCCDs could represent a suitable solution combining the key features of CDs together with the reduced environmental footprint of BC. The positive BCCDs performances achieved for inorganic species detecting and quantification outperformed even the most accurate and sensible traditional methods such as chromatographic approaches.

Organic detection is far from being simultaneously qualitative and quantitative but BCCDs development has room for improvement.

Accordingly, we believe that BCCDs use for sensing will be one of the game changing approaches in analytical chemistry, moving us toward a major breakthrough in the scientific community.

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