A True Biomass Standout: Preparation and Application of Biomass-Derived Carbon Quantum Dots

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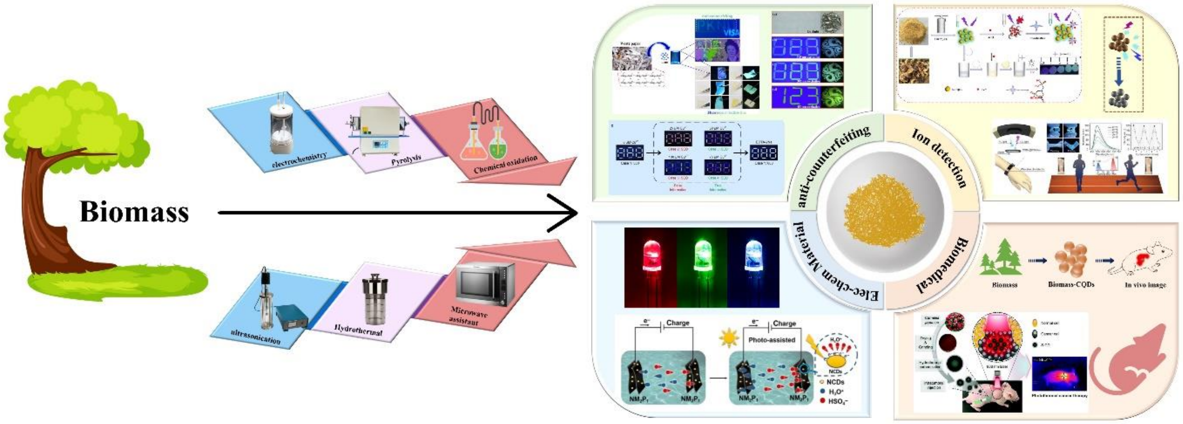

A True Biomass Standout: Preparation and Application of Biomass-Derived Carbon Quantum Dots

Xuedi Yang,[a] Shiyu Fu,[a,b,]* Altaf H. Basta,[c] and Lucian Lucia [d]

Carbon quantum dots (CQDs) are an emerging type of multifunctional nanomaterial. They have unique optical and electronic properties based on their quantum size effect and limiting effect. The carbon quantum dot prepared from biomass is green and environmentally friendly, and it can also achieve a high comprehensive utilization of undervalued biomass wastes. Biomass carbon quantum dots with abundant surface functional groups and good biocompatibility show great potential in ion detection and bioimaging. This review paper focuses on the synthesis methods of CQDs from biomass and the perspective of their applications in recent years, as well as the challenges in the future.

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Keywords: Carbon quantum dots; Biomass; Nanomaterial; Synthetic method; Application

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INTRODUCTION

Carbon Quantum Dots (CQDs) were first discovered in 2004 in the process of preparing single-wall carbon nanotubes by an arc discharge method (Xu *et al*. 2004; Baker and Baker 2010). CQDs are a type of well-dispersed spherical nanomaterial with all its dimensions below 10 nm. Compared with traditional semiconductor quantum dots, carbon quantum dots not only have the same advantages such as high quantum yield, adjustable emission wavelength as traditional semiconductor quantum dots, but they also have good photostability, low cytotoxicity, good biocompatibility, easy surface modification, and high chemical inertness, all of which have attracted extensive attention. Thus far, CQDs have been widely applied in many fields, such as cell imaging (Zhang *et al*. 2019; Rees *et al*. 2020), drug delivery (Rees *et al*. 2020), fluorescence detection (Haque *et al*. 2021), fluorescent light-emitting diodes (LEDs), catalysis (Li *et al*. 2018), energy conversion, and energy storage (Xu *et al*. 2020).

Considering global carbon emissions, biomass, which is known for its green environmental qualities and wide availability, has become the primary choice for carbon quantum dot carbon sources (Megía *et al*. 2021; Gupta *et al.* 2022). Biomass mainly includes lignocellulosic biomass, domestic waste, and livestock manure. It is mainly composed of cellulose, hemicellulose, and lignin, which are renewable, low cost, and abundant (Rodias *et al*. 2019; Sanoja-López *et al*. 2023). Moreover, lignocellulosic fibers, especially lignin, contain a high number of carbon skeleton structures with benzene rings, and contain various heteroatoms. Therefore, biomass is an ideal raw material for the preparation of quantum dots.

Of course, the chemical structure and component content of different lignocellulosic biomass are different, which makes accurate preparation and the regulation process of CQDs difficult, resulting in complex preparation methods and low mass yield and quantum yield (Arul *et al*. 2023). Therefore, exploring the formation mechanism of CQDs is of great significance for the development of efficient preparation methods and targeted regulation means. In view of this, with lignocellulosic biomass as the starting point, the preparation methods, influencing factors, and applications of CQDs are reviewed, with a focus on the formation and transformation mechanism of CQDs, as shown in Fig. 1. The application and development of CQDs optical properties are summarized and analyzed.

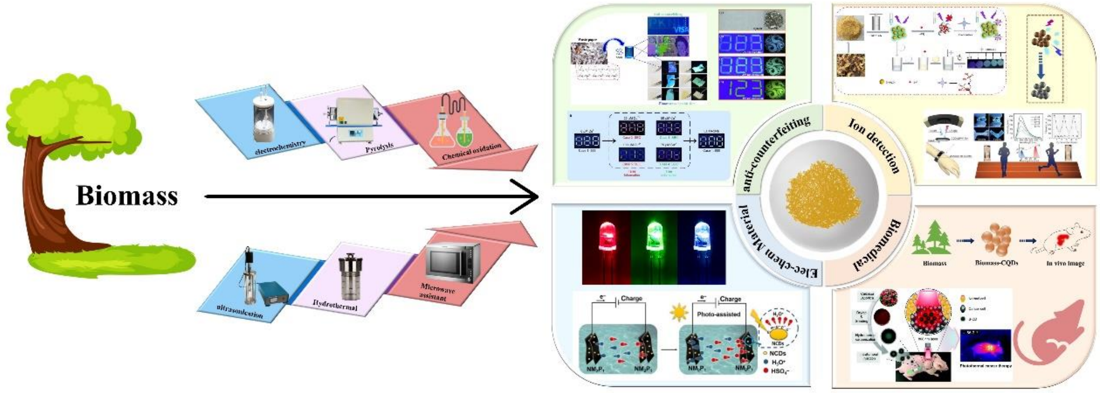

Fig. 1. Preparation method and application diagram of biomass carbon quantum dots

BIOMASS CARBON QUANTUM DOT

Chemical Structure of Biomass Carbon Quantum Dots

In the past, CQDs prepared from biomass were usually composed of amorphous and crystalline carbon nuclei with defects on the surface. Its main components are C, H, O, N, S, and P, in which the heteroatoms often appear as doping atoms. CQDs are generally spherical with a relatively clear lattice. The interlayer distance is approximately 0.2 to 0.34 nm (Edison *et al*. 2016). CQDs have sp2 carbons as its core and surrounded by rich oxygen-containing functional groups, such as hydroxyl, carboxyl, and carbonyl groups. However, from a suite of synthetic routes, various heteroatoms and functional groups are introduced, and various defects (defect states, surface states, edge states) on the surface of carbon nuclei, as well as the structure and physical and chemical properties of carbon quantum dots are introduced (Zheng *et al*. 2014).

Optical Properties of Carbon Quantum Dots

The optical properties of CQDs usually include light absorption properties, light stability, pH dependence, excitation dependence, up conversion luminescence, *etc*. The phenomenon that CQDs emit photons of higher energy and shorter wavelength under the excitation of multiple photons of lower energy and longer wavelength is called up conversion photoluminescence (PL) (Cao *et al*. 2007; Cong and Zhao 2017; Lou *et al*. 2022). Most biomass CQDs PL emission wavelengths are within the range of 400 to 500 nm; they are related to size and surface chemical composition, but also excitation wavelength. CQDs usually have strong absorption at 210 to 360 nm (UV region) (Guo *et* *al*. 2016; Aziz and Ramzilah 2019; Gao *et al*. 2020; Nafchi *et al*. 2022), whose absorption bands at ~ 230 nm and 300 nm belong to the π-π* transition of the C = C or the n−π* transition of C = O/C = n (Cong and Zhao 2017; Murali *et al*. 2021). Absorption in the ultraviolet region is a feature of CQDs and is critical for a variety of applications such as photovoltaics, photocatalysis, and fluorescence (Zhang *et al*. 2018; Madhi and Hadavand 2022). The absorption properties of CQDs are also related to size, functional group, excitation wavelength, and dopant.

According to precedent, CQDs demonstrate low cytotoxicity and good biocompatibility (Lim *et al.* 2015; Chung *et al*. 2021; Lin *et al*. 2022). Zhang *et al.* (2018) prepared CQDs using coffee bean shells, in which mice survived after 6 days of injection. In addition, relevant results show that the fluorescence properties of quantum dots do not change after several hours of ultraviolet irradiation, while the fluorescence intensity of CQDs dispersed in water is nearly unchanged at room temperature for a long time, and fluorescence stability is very good. They have a broad application prospect in bioimaging and bio-detection.

There are abundant oxygen-containing functional groups on their surfaces, such as hydroxyl, carboxyl, carbonyl, and so on. Under certain circumstances, they can form stable quantum dot complexes with amino acids, metals ions, and other coordination, and some of the binding is reversible. This property of biomass CQDs can be used as a fluorescence sensing probe (Kang *et al*. 2020; Ye *et al*. 2022).

PREPARATION METHOD

With the advent of more advanced CQDs, various preparation methods are continually emerging, which can be classified as “top-down” and “bottom-up” methods, and several preparations use these methods comprehensively. The “top-down” approach is to decompose a larger carbon structure into quantum-sized materials by means that include oxidative cutting, physical stripping, or a combination of grinding and cutting. In the bottom-up method, small molecular organic matter is converted into CQDs by pyrolysis, templating, microwave-assisted synthesis, *etc.* (Dong *et al*. 2019; Surendran *et al*. 2019; Kamble *et al*. 2022). These methods are suitable for small molecule precursors and have attracted increased attention in recent years. The “bottom-up” method is the most common way to prepare CQDs from natural products, from which the components are not separated (Meng *et al*. 2019; Zhu *et al*. 2022 a). However, a growing number of researchers combine these two methods. First, chemical methods are applied to extract precursors from natural biomass. Then, the CQDs are prepared by hydrothermal heteroatom doping or surface modification. Hydrothermal synthesis offers a fast and energy-efficient single-step approach using low-cost biomass carbon sources like glucose. This method stands out for its efficiency and scalability (Wang *et al*. 2023). Moreover, the electrochemical method has been widely reported for CQD synthesis due to its tunability in particle size and photoluminescence performance (Wang *et al*. 2019a).

Pyrolysis Method

The pyrolysis method is to heat lignocellulosic raw materials at high temperature under an inert atmosphere or hypoxic conditions, promote their decomposition into small molecular compounds, and then synthesize CQDs through cross-linking condensation and other reactions (Kang *et al*. 2020). For example, cellulose and lignin can be used as carbon sources to prepare carbon points at 200 to 400 °C by solvent-free pyrolysis (Chen *et al*. 2022). Cellulose CQDs prepared at 300 °C and lignin CQDs prepared at 350 °C showed high quantum yields of 11.7% and 23.4%, respectively, which is consistent with the high degree of graphitization. At the same time, a comparison of CQDs prepared by solvothermal synthesis with the same raw material, the experimental results show that CQDs prepared by hydrothermal method have more C-O than CQDs prepared by solvent-free method with water solvent in carbonization. Carbon dots prepared by solvent-free pyrolysis have better conjugate carbon core structure (sp2 carbon) and better fluorescence quantum yield than those prepared by solvent-thermolysis.

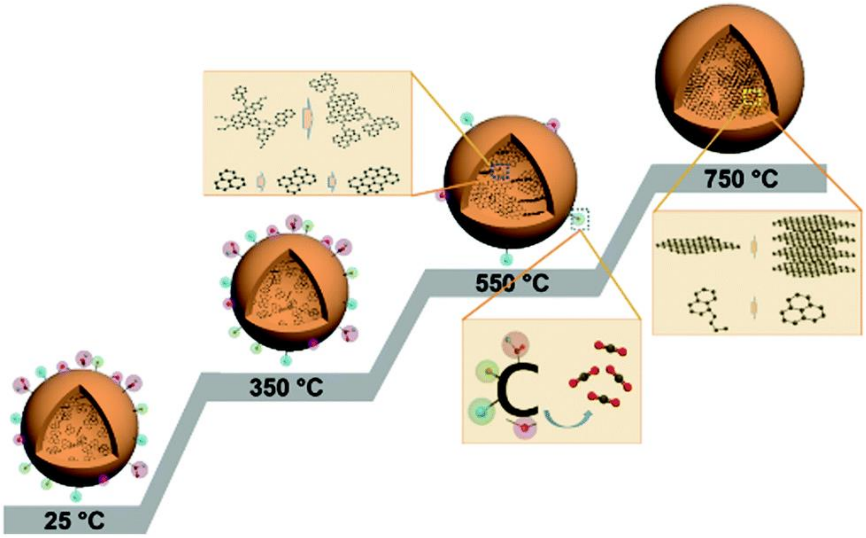

Fig. 2. Illustration of structural evolution process of CQDs under thermal treatment. (Luo *et al*. (2022); Reprinted with permission from Royal Society of Chemistry)

Luo *et al.* (2022) used glucose as carbon source to prepare CQDs by one-step hydrothermal method (200 °C, 12 h), and further carbonized them under nitrogen at 350 °C, 550 °C, and 750 °C to study the structural evolution of CQDs during pyrolysis. They found that the morphology and chemical structure of CQDs remained basically stable at 350 °C, while the weakly bonded oxygen functional groups (C=O and -COOH) almost disappeared when the carbonization temperature increased to 550 °C. Conjugated sp2 carbon atoms were ordered into aromatic clusters, and the proportion of sp2 hybrid carbon atoms increased from 65% to 82%. After heating to 750 °C, most of the oxygen groups were removed, and the degree of graphitization of CQDs further increased, forming a highly crystalline structure. The specific process is shown in Fig. 2. The optical characterization results of this type of CQD show that its behavior in near infrared (NIR) solid PL is similar to that of solid graphene oxide (GO).

With the deepening level of research on biomass quantum dots, machine learning, a powerful technology based on comprehensive data analysis, has also been applied to optimize the pyrolysis and preparation conditions of biomass carbon quantum dots. Chen *et al*. (2023) used 10 kinds of agricultural wastes rich in lignocellulosic fiber, such as wheat straw (WS), corn straw (CS), and bamboo stalk (BS), as carbon sources. The CQDs were prepared by pyrolysis at 300 to 500 °C under limited oxygen conditions for 2 to 8 h. With the GBDT-R model for analyzing the importance of characteristics, it was found that the process parameters of biochar production had the greatest influence on QY, which exceeded the influence of raw material properties. The specific research is shown in Fig. 3. The effects of pyrolysis temperature, nitrogen content, residence time, and carbon-nitrogen ratio on the prediction accuracy of QY were determined as 47.68%, 18.8%, 16.84%, and 16.7%, respectively. When the author used these four eigenvalues to predict and verify the dataset, the relative error between the predicted QY value and the experimental QY value was 0 to 4.60%. The smallness of these values is favorable for the future development and utilization of biomass quantum dots and the combination of artificial intelligence analysis.

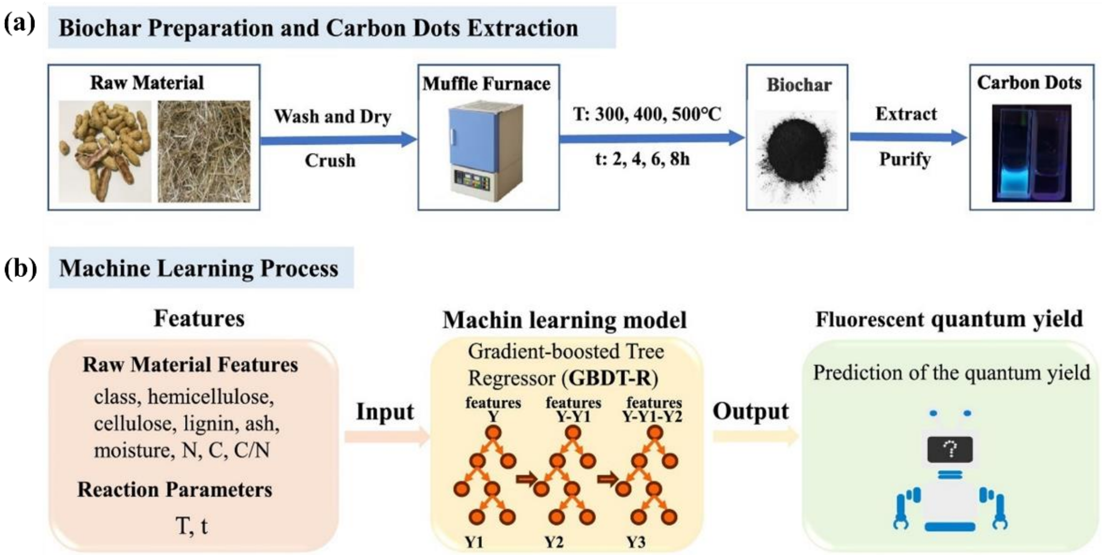

Fig. 3. Machine learning assisted biomass CQDs synthesis: (a) Extract CQDs from biochar to build a training dataset for machine learning; (b) Using machine learning models to predict the Quantum Yield (QY) of CQDs extracted from biochar. (Chen *et al*. (2023); Reprinted with permission from Elsevier)

Solvothermal Method

Solvothermal method refers to convert insoluble substances in water or other solvent to CQDs in one step under high temperature and high pressure. Similar to all chemical reactions, reaction time, temperature, and solvent system for preparation of carbon quantum dots are the three key parameters regulating the mean particle size and QY. Studies on the preparation of biomass quantum dots by hydrothermal method in recent years are listed in Table 1. Among the solvents, water solvent accounted for about 64% (Palacio-Vergara *et al*. 2023). Li *et al.* (2019) prepared CQDs from poplar leaves in kilogram level, which is expected to achieve large-scale commercial preparation of biomass carbon quantum dots.

The preparation of CQDs from crop biomasses is typically carried out *via* hydrothermal treatment. As a carbon source, the proportions of biomass components, such as cellulose, hemicellulose, and lignin, seriously affect the formation of CQDs (Ding *et al*. 2021). The process of preparing biomass CQDs by hydrothermal method is shown in Fig. 4. Liu *et al.* (2020) found that in the hydrothermal process of cellulose, hydrogen bonds and glucoside bonds in cellulose were first broken to form intermediates, such as oligosaccharides, and the intermediates underwent dehydration and rate-opening reactions of pyran to produce small molecules including hydroxy acetaldehyde and 5-

hydroxymethylfurfural. The polysaccharides and small molecules underwent cross-linking and condensation, and hydrothermal carbonization to produce CQDs. When alkali lignin is used as raw material, the transformation path of alkali lignin to intermediates is that lignin breaks ether bonds under acid catalysis and forms lignin nanoparticle intermediates, which are aromatized by dehydration condensation to form larger aromatic clusters, and then form CQDs by π-π superposition and carbonation nucleation (Zhu *et al*. 2021 a; Zhu 2022 b). Chai *et al.* (2019) found that the formation of sp2 hybrid conjugated carbon nuclei in CQDs was related to the lignin with polyaromatic ring structure by hydrothermal carbonization process to obtain CQDs from bagasse. The macromolecules, such as polysaccharides, in bagasse may attach to the outer layer of CQDs and give it rich oxygen-containing groups. However, according to Wu *et al*. (2021), hemicellulose leached from cellulose and lignin are more likely to be hydrolyzed into small molecules and then to CQDs through a bottom-up method. The mass yield of CQDs prepared from flax stem, peanut shell, and bamboo was lower than 10%, mainly because corn cob was rich in hemicellulose and cellulose, and its texture was loose, which was conducive to hydrolysis and carbonization, while oligosaccharides and monosaccharides of hydrolysis products were the main raw materials for CQDs synthesis. In addition, in the process of preparing CQD from corn cob at different times (8 to 16 h) and temperatures (160 to 220 °C), the yield gradually decreased with the extension of time, and the yield also gradually decreased with the change of temperature at a fixed time.

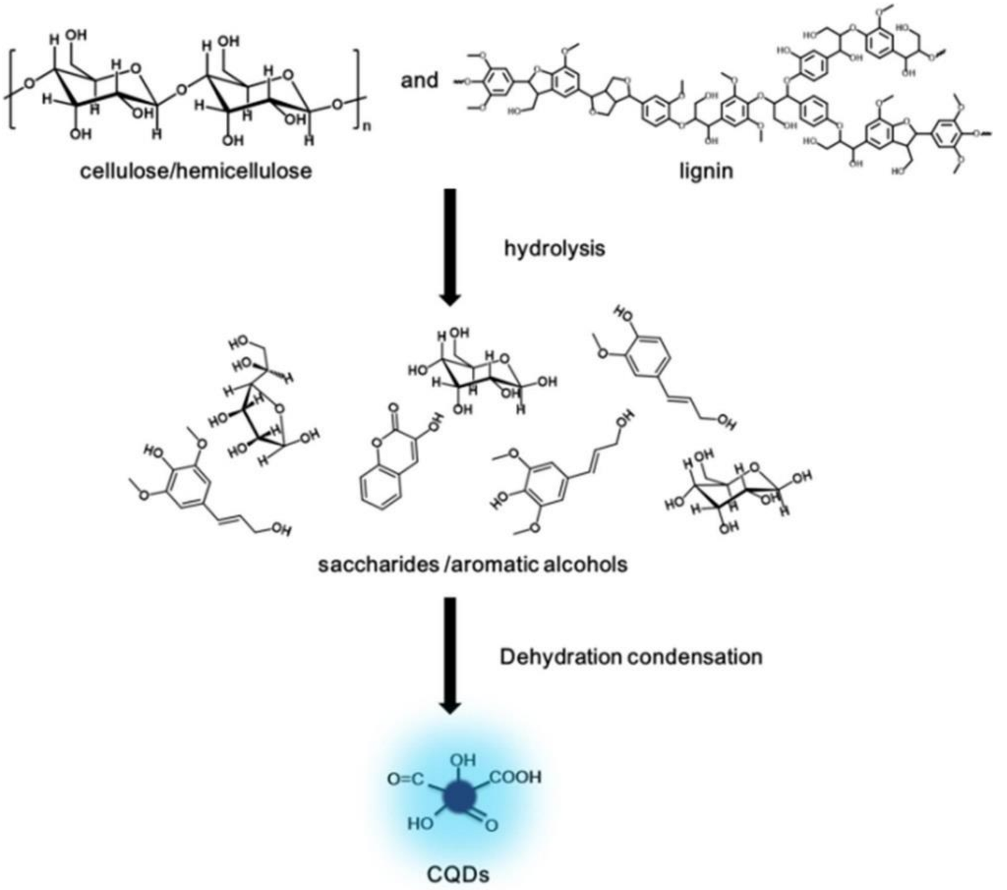

Fig. 4. Preparation procedure for CQDs from biomass *via* hydrothermal treatment (Ding *et al*. (2021); Reprinted with permission from Elsevier)

Zhao *et al*. (2023) used olive leaves as raw material and acetone as solvent to prepare near infrared fluorescence emission carbonized polymer points with QY up to 71.4% by the hot solvent method. The excitation and emission ranges are 398 to 428 nm and 650 to 780 nm, respectively. In addition, its characterization showed that there was no N element in CQDs, but aggregates formed by the stacking of heterocyclic and aromatic rings containing O. *In vivo* studies showed that the fluorescence signal was still obvious in small animals after 10 h injection of CQDs, with long-term surface retention time and no toxicity. The authors speculate that it may be excreted in the intestine by the renal system or metabolized by the liver.

Table 1. Summary of Carbon Sources and Solvothermal Methods of Biomass-derived CQDs

Carbon Source	Solvothermal Condition	Doping Element	QY (%)	Application	Reference
Wheat straw	250 °C, 10 h	N	20	Labeling, imaging and sensing	Yuan *et al*. (2015)
Tobacco leaves	200 °C, 3 h	-	27.9	Tetracyclines detection	Miao *et al*. (2018)
Durian flesh	150 °C, 12 h	S	79	Cell imaging	Wang *et al*. (2018)
Rice residue	200 °C, 12 h	-	23.48	Detection of Fe^{3+} ions, tetracyclines	Qi *et al*. (2019)
Wheat straw and bamboo residues	180 °C, 4 h	N	13	Cell imaging, in vivo bioimaging	Huang *et al*. (2019)
Cellulose	140-300 °C, 1-24 h	N	10.9	Detection of Fe^{2+}	Su *et al*. (2019)
Alkali lignin	200 °C, 12 h	N, S	21	Detection of H_2O_2	Wang *et al*. (2019b)
Magnolia flowers	200 °C, 8 h	-	8.13	Detection of Fe^{3+}	Wang *et al*. (2020)
Prehydrolyzed lignin	220 °C, 11 h	S	13.5	Detection of Sudan I	Yang *et al*. (2020)
Alkali lignin	200 °C, 12 h	N, S	30.6	Anti-Counterfeit	Zhu *et al*. (2021 b)
Alkali lignin	200 °C, 12 h	N, B	7.4	Anti-Counterfeit	Gu *et al*. (2022)
Mopan persimmons	150 °C, 4 h	-	8.39	Anti-Counterfeit and detection of Fe^{3+}	Ma *et al*. (2022)
Grape skins	200 °C, 8 h	N	15.3	Detection of tetracyclines	Tang *et al*. (2022)
Tobacco leaves	220 °C, 12 h	N	13.7	Tetracycline testing	Liang *et al*. (2022)
Orange peels	700 W and 220 °C, 0.5 h	-	-	Electrode material	Olmos-Moya *et al*. (2022)
Laurel leaves	180 °C, 5 h	N	49.9 (ETH)	Anti-counterfeiting	Long *et al*. (2023)
Mango skin	Microwave	N,P	14.3	Antibacterial	Hua *et al*. (2024)

Lignin-based carbon quantum dot has attracted increased attention. Wu *et al.* (2023) successfully prepared CQD from lignin using γ-valerolactone (GVL) and water as binary solvents. Through adding doping reagents, urea and citric acid, in lignin solution, the luminescence fluorescence of CQD was changed from blue to yellow, and the fluorescence performance was significantly improved, and the maximum quantum yield could reach 33.2%.

Wang *et al*. (2023 a) prepared multicolor fluorescent biomass CQDs by applying a solvothermal method that included water, ethanol, and an ethanol/acetone mixture. The biomass CQDs generated were able to emit a spectrum of colors including blue, crimson, grayish white, and red that displayed quantum yields of 8.9%, 12.3%, 10.8%, and 14.4%, respectively. It was found that the luminescence was affected by solvent boiling point and polarity. These factors, in fact, are prominent in mitigating carbonization. With respect to the three solvents and mixtures employed, water has the highest boiling point and acetone the lowest. If the preparation conditions were maintained constant, it was determined that there was an inverse relationship between the boiling point (BP) and carbonization time, in which lower BPs and longer carbonization time gave rise to larger diameter CQDs.

Microwave-Assisted Method

The microwave-assisted method employs a fast-heating precursor, which contributes to low cost and high efficiency technology to prepare CQDs. Zhu *et al.* (2009) prepared CQDs in a few minutes from polyethylene glycol and sugar solutions (glucose, fructose, *etc.*) in a 500 W microwave oven. Liu *et al.* (2020) obtained CQDs with the use of soybean meal as raw material by microwave hydrothermal method. In this process, the rich protein of soybean meal is first hydrolyzed into amino acids, and then through decarboxylation and deamination reactions, amines and low molecular weight organic acids are produced, respectively. These intermediate products are then cross-linked and condensed with cellulose hydrolysates to form CQDs. Architha *et al.* (2021) successfully synthesized blue-emitting CQDs from Mexican peppermint leaves by a microwave-assisted reflux method. The fluorescence quantum yield of CQDs obtained was 17%, with good water solubility and fluorescence intensity. The product showed excellent performance in biological application and detection of Fe^{3+}. The microwave-assisted method entails breakage of chemical bonds within the biomass material itself, and then the material is dehydrated, polymerized, and finally carbonized to form carbon nanostructures driven by the microwave energy. Compared with traditional methods, such as solvothermal method and pyrolysis method, the microwave-assisted method can greatly shorten the reaction time typically within a few minutes. It has relatively low requirements for equipment and has high energy utilization efficiency, so it has received increasing attention. However, it is reported that its controllability is poor and the particle size distribution of the prepared CQDs is not uniform.

APPLICATIONS

Biochemical Sensing and Detection

Biomass CQDs has advantages, such as good fluorescence stability, low cost, and specific structured or functionalized CQDs with a fluorescence quenching effect when encountering certain metal ions, small molecules, or pH changes (Yang *et al*. 2016; Kundu *et al.* 2022). The target substance can produce a strong binding force or chelation with some functional groups on the surface of CQDs, and have high selectivity and sensitivity, resulting in fluorescence quenching of CQDs (Das *et al*. 2019; Zhang *et al*. 2019; Chang *et al*. 2022; Wang *et al*. 2023 b). These aspects are shown as Fig. 5(a). Therefore, the fluorescent CQDs can be applied to configure a low-cost, simple, efficient, and rapid analysis fluorescence sensor with quantitative detection of some target substances, which may be superior to traditional detection methods. George *et al.* (2023) synthesized CQDs from papaya seed through a microwave-assisted carbonization process with the yield of 9.7%. It was able to selectively detect Fe^{3+} and had a limit of detection (LOD) value of 2.35 μM. Xu *et al*. (2019) obtained CQDs from Maojian tea and Longjing tea *via* hydrothermal method with antioxidant capacity and special response ability to Hg^{2+}, which were successfully applied to the detection of Hg^{2+} in rice. The detection minimum was as low as 6.32×10^{-9} nmol/L. The response range was 2.00×10^{-7} - 6.00×10^{-5} mol/L, which provides a great potential in the fields of food, medicinal, and environmental monitoring.

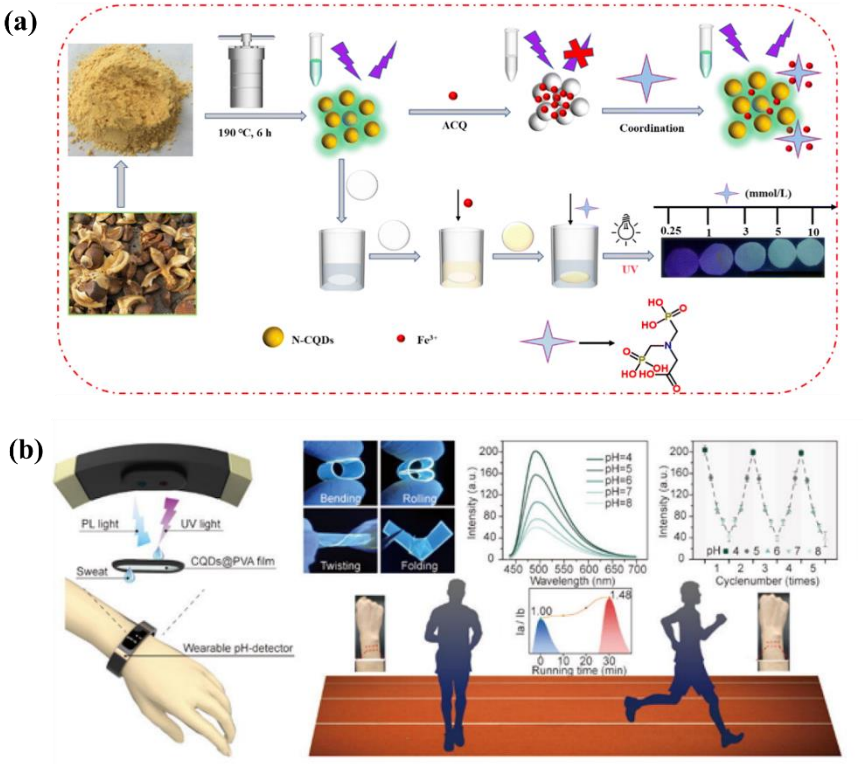

Fig. 5. (a) Schematic diagram of CQDs fluorescent probe for detecting glyphosate (Wang *et al.* (2023 b); Reprinted with permission from Royal Society of Chemistry); (b) CQDs@PVA Schematic diagram of the fluorescent film smart pH sensor (Tao *et al*. (2022); Reprinted with permission from Elsevier)

Column chromatography can also be used to collect carbon quantum dots. Ma *et al*. (2022) prepared carbon quantum dots (MP-CQDs) from local fruit Mopan persimmons *via* hydrothermal method for collection by silica column chromatography. The obtained MP-CQDs were in size of 3.18 ± 0.69 nm, which can be well dispersed in the aqueous solution. Calcium ions (Ca^{2+}) play a crucial role in signal transduction pathways associated with various physiological and pathological events. Chen *et al*. (2018) reported quantum dots from chili peppers as fluorescence reporter molecules for intracellular Ca^{2+} imaging, based on internal filter-mediated luminescence, supplemented by Ca^{2+} chelated alizarin red

S (ARS). The absorption of the Ca-ARS complex is redshifted and exhibits poor internal filtration. Therefore, Ca^{2+} can be detected by internal filter-mediated luminescence using the CQDs nanohybrid system, and imaging of intracellular Ca^{2+} and real-time monitoring of changes in Ca^{2+} levels under histamine stimulation are also achieved. Zhang *et al.* (2019) obtained nitrogen-doped CQDs from lignin with exciting bright green fluorescence, which is sensitive to Ag^{+} with a detection threshold of only 0.35 μmol/L.

Tao *et al.* (2022) used biomass-derived CQDs from natural lignocellulose, which was loaded on poly(vinyl alcohol) (PVA) as CQDs@PVA composite membrane, as shown in Fig. 5(b). The obtained membranes exhibited high transparency (light transmittance 88%), excellent mechanical flexibility (tensile strength 39.7 MPa, elongation at break 453%) and excellent fluorescence properties. An intelligent pH detector based on the fluorescent film, which exhibited high stability of green fluorescence and showed sensitive pH responsiveness, was designed for real-time sensing and detection of pH changes in sweat during human movement. In the future, more biomass quantum dot composites can be applied in wearable, real-time health monitoring and other fields.

Biomedical

Arul *et al*. (2023) synthesized doped CQDs, which could easily penetrate the HeLa cell wall and diffuse in the cell uniformly. Bright HeLa cell images were obtained at 410 nm, 480 nm, and 580 nm excitation regions, which is shown as Fig. 6(a). Xue *et al*. (2019) hydrothermally treated alkali lignin, citric acid, and ethylenediamine to obtain CQDs with a quantum yield of 43%. The CQDs could emit light stably in the range of 454 to 535 nm under the excitation of 375 to 460 nm wavelength light source. At the same time, it had good cytocompatibility and could "shield the nucleus" to realize multicolor fluorescence endoscopy of cervical cancer cells.

Zhao *et al*. (2019) obtained boron nitride quantum dots with a maximum quantum yield of 18.2% from recovered lignin and boron oxide at a high temperature of 200 to 500 °C, which can stably excite bright blue fluorescence in the ultraviolet region with a size of 0.52 to 2.25 nm. Human breast cancer cells (MCF-7) added with 100 mg/mL of this quantum dot showed a cell survival rate of more than 92 % after 24 h of culture, which can be used as a potential biological imaging material.

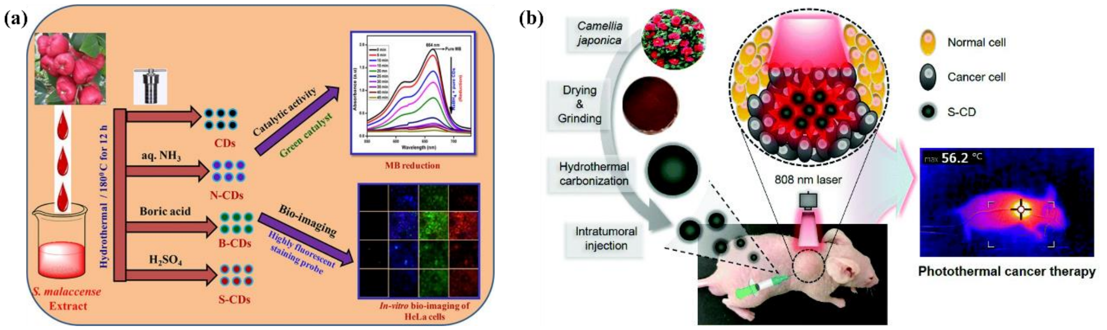

Fig. 6. (a) Bio-imageable multicolor CQDs prepared from S*. malaccense* (Arul *et al*. (2023); Reprinted with permission from Elsevier; (b) Schematic illustration of S-CD preparation and photothermal cancer therapy (Kim *et al*. (2021); Reprinted with permission from Royal Society of Chemistry)

Because CQDs exhibit excellent biocompatibility and low cytotoxicity, many types of CQDs are used in photothermal therapy (PTT). Kim *et al*. (2021) prepared sulfur-doped

CQDs using *Camellia japonica* flowers with strong NIR absorbance. The optimal low-dose (45 ug mL^{-1}) was obtained at medium laser power (808 nm, 1.1 W cm^{-2}). The photothermal conversion efficiency is as high as 55.4%, which can safely and effectively treat cancer, shown as Fig. 6(b).

Anti-counterfeit

Wang *et al*. (2023 c) used four kinds of biomass CQDs obtained through different solvent systems as fluorescent inks, and obtained different multi-color patterns through inkjet printing, which has a good anti-counterfeiting effect. This study provided a low-cost and simple green synthesis strategy for multicolor luminescent biomass CQDs, which indicates that biomass CQDs have broad application prospects in ion detection and advanced anti-counterfeiting.

Carbon quantum dots with low toxicity, unique optical properties, and excellent chemical stability were synthesized by heating wastepaper in different solvents (water, ethanol, and 2-propanol) using traditional solvothermolysis (Park *et al*. 2020). In the later stage of the experiment, the optical properties of carbon quantum dots were rationally used to make anti-counterfeited ink and fluorescent flexible film, as shown in Fig. 7(a).

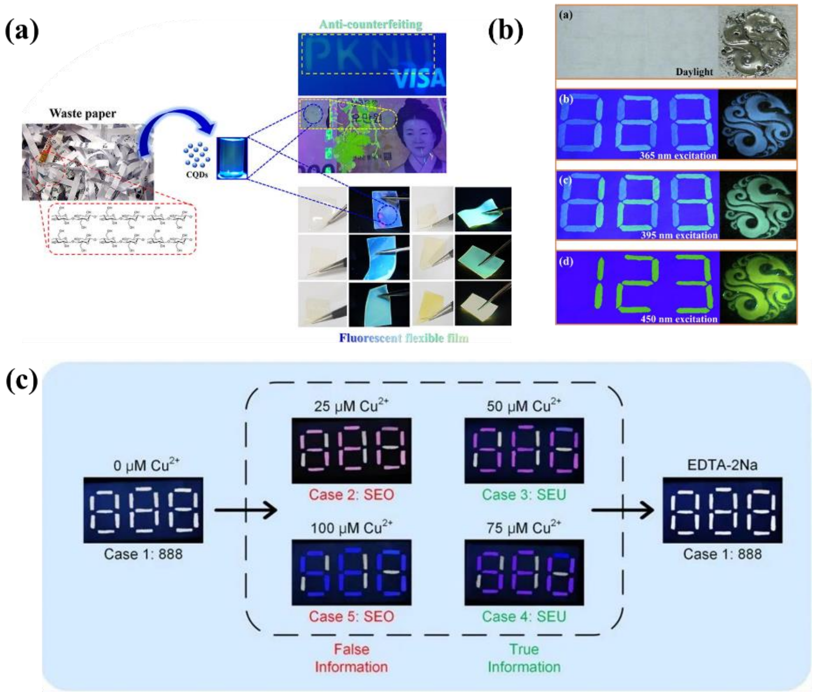

Fig. 7. (a) Photos of the CQDs security marks used on banknotes under daylight, 365 nm, and 405 nm light (Park *et al*. (2020); Reprinted with permission from Elsevier); (b) Photos of the anti-counterfeiting patterns and gelatinoid MP- CQDs@sugar under daylight, 365, 395, and 450 nm excitation (Ma *et al*. (2022); Reprinted with permission from Elsevier); (c) The invention relates to a CQDs@MOF-nano-fiber film combination anti-counterfeiting device (Zhao *et al*. (2023); Reprinted with permission from Wiley)

Such a method can be applied to information protection, flexible recognition, and other fields. The excitation dependence of quantum dots can also be applied to anti-counterfeiting purposes. Ma *et al*. (2022) used the obtained biomass quantum dots combined with commercial fluorescent ink to draw anti-counterfeiting patterns. The product showed different fluorescence at different excitation wavelengths (Fig. 7(b)), such that it can be applied to the field of anti-counterfeiting.

The signal "888" anti-counterfeiting pattern with white fluorescence was designed using CQDs@MOF nanofiber electrospinning film with different sensitivity to Cu^{2+}, shown as Fig. 7(c). When the fluorescent label is in contact with a specific concentration of Cu^{2+} solution, the true information is displayed. False information will be displayed at lower or higher Cu^{2+} concentrations. When the fluorescent label was treated with EDTA-2Na, the original white fluorescent "888" pattern was restored (Zhao *et al*. 2023).

Although biomass carbon quantum dots have broad application prospects in anti-counterfeiting, the following problems may exist in the actual research and application process. To begin with, the complex preparation process leads to a high cost. The preparation of biomass carbon quantum dots needs to go through a series of complex chemical reactions, which not only takes a lot of time and resources, but it is difficult to ensure that each step can achieve the ideal effect. Most of the current research is limited to the laboratory stage, and there is still a long way to go to commercialization. Additionally, although biomass carbon quantum dots have good optical properties, because of their short life and changes in stability in different environments, their application effect in anti-counterfeiting labels may be affected. Therefore, solving the above problems requires continuous research and the support of advanced technology.

Composite Electro-chemical Material

The small particle size, abundant edge sites, and many functional groups of biomass CQDs make them promising candidates for high-performance electrode materials in supercapacitors (Prasath *et al*. 2018; Thangaraj *et al*. 2021; Ansari 2022). Furthermore, the use of biomass residues to obtain carbon electrodes with different electrochemical properties has been demonstrated, highlighting the successful application of biomass CQDs in high-performance supercapacitors (dos Reis *et al*. 2020). The synthesis of carbon quantum dots from natural sources and their use to improve the performance of supercapacitors in other materials further supports the potential of biomass-derived quantum dots in energy storage applications (Sahoo *et al*. 2018). The review by Wareing *et al.* highlights the use of biomass-derived quantum dots in the electrical field, further highlighting their potential for supercapacitor applications (Wareing *et al.* 2021).

Researchers have used the hybrid fiber based on $Ti_3C_2T_X$ loaded CQDs. A photo-assisted charging fiber supercapacitor was fabricated, as shown in Fig. 8 (Wang *et al*. 2021). Compared with the optical fiber without CQDs, the optical absorption, charge transfer rate, and charge transfer kinetics of the optical fiber were improved *via* addition of CQDs with good photosensitivity. The ability of light-enhanced capacitance under the condition of light-assisted charging has been shown.

Oskueyan *et al.* (2020) used carrot juice as a biomass carbon source to prepare carbon quantum dots *via* hydrothermal method, and then they prepared polyaniline-carbon quantum dots using an *in-situ* polymerization method. A high-potential supercapacitor was prepared by mixing CQDs composite material with polypyrrole-graphene. The nanocomposite exhibited the best electrochemical performance with a maximum specific capacitance of 396 F^{-1}. The specific capacitance could still reach 62% of the initial capacitance after 1000 cycles and maintain 65% of the specific capacitance. This work provides a new class of bi-functional nanocomposites for supercapacitors.

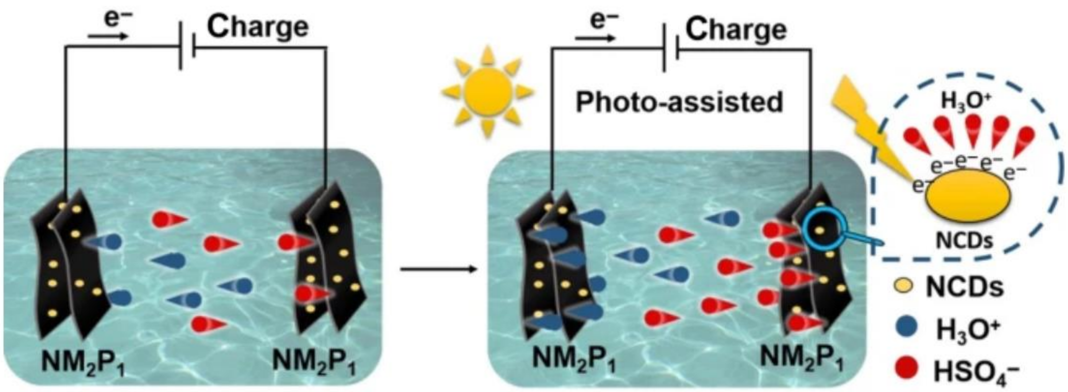

Fig. 8. $Ti_3C_2T_x$-based hybrid fibre modified by nitrogen-doped CQDs used as supercapacitor (Wang *et al*. (2021); Reprinted with permission from TSINGHUA UNIV PRESS)

Although there are some challenges in the research of biomass carbon quantum dots in energy storage, such as quantum efficiency and defect density, their characteristics of non-toxicity, sustainability, and low cost give them broad application potential. At present, researchers are working hard to solve these problems to promote the commercial application of biomass carbon quantum dots.

CONCLUSION AND PERSPECTIVES

Challenges of Synthesis

At present, many studies on biomass CQDs are prepared using food and other valuable bioresources, and most of the "top-down" synthesis will produce a large number of by-products, resulting in a lot of waste of biological resources in the one-step process. How to best deal with these remaining by-products remains a challenge.

Impacts of Carbon Sources

Due to the complex structure and composition of biomass resources, there are many small molecules and inorganic substances. The role of these components in the formation of CQDs has not been clarified, thus demanding further exploration.

Broaden Optical Performance

To date, the absorption and emission wavelengths of biomass CQDs prepared in most studies are usually in the ultraviolet/visible region, which cannot penetrate deep tissues for light imaging. In biomedical applications, NIR light is superior to ultraviolet/ visible light because it can penetrate deep into tissues and has low biological toxicity. In the perspective future, it is necessary to develop the carbon quantum dots with the absorption and emission wavelengths in the range of long wavelengths, such as NIR, to fit medical applications.

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