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CARBON DOTS: SYNTHESIS METHODS, PROPERTIES AND CHEMICAL SENSING APPLICATIONS

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ABSTRACT

Carbon dots (CDs) are a novel class of fluorescent nanoparticles and carbon nanomaterials with outstanding physical, chemical properties and biocompatibility, which have attracted worldwide attention and have been applied to every branch of applied sciences from the beginning of this millennium. In this article, we have reviewed the recent progress made in this newest member of carbon nanomaterials, focusing on their synthetic strategies namely top-down and bottom-up methods. In addition, their properties including morphology and structure, compositions, optical properties (absorbance, photoluminescence properties, quantum yields and luminescence mechanisms) have been presented. For the applications of this newest member of fluorescent nanoparticles, CDs both with and without being functionalized recognition elements are selective and sensitive for sensing of analytes, including metal ions (e.g., Hg^{2+}*,* Cu^{2+}*,* Pb^{2+}*), non-metallic ions (e.g. sulfide ions, pyro phosphate ions, sulphite) and small organic molecules (e.g., bisphenol A, dihydroxy benzene, hydroquinone) have been reviewed. Also, the proposed fluorescence sensing mechanism of CDs have been outlined for the explanation of effectively selective and sensitive detections of inorganic ions and small organic molecules of CDs.*

Keywords: *carbon dots (CDs); top-down method; bottom-up method; fluorescence; chemical sensing; inorganic ions; organic molecules.*

1. INTRODUCTION

Carbon dots (CDs), the newest member of carbon nanomaterials having average diameter less than 10 nm have emerged as the most precious gifts in nanotechnology because of their magical properties and applications [1,2]. They are also known by different names including carbogenic nanoparticles, carbon nanoparticles (CNPs), carbon quantum dots (CQDs), carbon nanodots (CNDs) or graphene quantum dots (GQDs). Comparing to conventional semiconductor quantum dots, organic agents, and other fluorescent sensors, CDs exhibit fascinating properties such as tunable fluorescence emissions, benign chemical compositions, facile synthesis, versatile surface modification and functionalization, and excellent photochemical and physicochemical stabilities [3]. Therefore, CDs have drawn attention from researchers worldwide and have also been referred to as carbon nanolights [3,4]. In addition, photophysical and chemical properties of CDs can be varied dramatically by tuning their shapes and sizes and also by doping heteroatoms such as nitrogen, phosphorus, sulfur, boron and so on [5,6]. Also, surface engineering plays a significant role in tuning their properties and diversifying their applications. For preparing CDs, both natural and synthetic organic precursors can be employed. Synthesis approaches that are frequently used in this concern are microwave irradiation, laser ablation, hydrothermal treatments, ultrasonic irradiation, electro chemical, arc discharge, and pyrolysis, to name but a few [7]. This short review specifically focuses on the synthetic methodologies of CDs and their sensing applications.

2. SYNTHETIC STRATEGIES

CDs were accidentally discovered by Xu et al. while purifying single-walled carbon nano- tubes (SWCNTs) derived from the arc-discharged soot in 2004 [8]. Shortly after, Sun et al. prepared the first stable photoluminescent (PL) carbon nanoparticles with different sizes, namely, “carbon quantum dots” - with improved photoluminescence - in both solution/liquid and solid states [9]. Later on, Cao et al. have explored the utilization of the surface-passivated CDs in multi-photon bio- imaging by internalizing them inside the human breast cancer MCF-7 cells, where these CDs have proved their capability to label both cell membrane and cytoplasm of the cancer cells [10]. Furthermore, in 2009, Yang et al. synthesized and consequently employed the surface-passivated CDs in *in vivo* mice model imaging [11]. Thereafter, numerous research works focusing on effective synthesis of CDs for various applications have been published.

Depending on the direction of size development of the starting materials, the synthesis of CDs can be generally divided into two kinds of approaches that are “top-down” and “bottom-up” approaches. Usually, “top-down” methods can utilize cheap bulk carbon materials as precursors and also can be applied to any graphitized materials; however, they often have relatively low production yield and require longer reaction time and not easily disposable strong oxidants. On the other hand, “bottom-up” methods can offer relatively high yield and quantum yields as well as the convenience to introduce heteroatom doping during synthesis pro- cesses.

2.1 Synthesis of carbon dots via “top-down” approach

The “top-down” approach, on one hand, fabricate CDs form bulk structures of carbon such as graphite, activated carbon, and carbon nanotubes by treatments such as arc discharge [8,12,13], laser ablation [9,14,15], electro-chemical oxidation [16-18], and chemical oxidation methods [19-28].

2.1.1 Arc discharge method

CDs fabricated by an arc discharge method had been an accidental event which was first reported by Xu et al. during synthesis of SWCNTs [8]. In this process, electrical dis- charge across two graphite electrodes results in the formation of small carbon fragments or CDs (Figure 1). In addition, CDs derived from pristine SWCNTs by means of an arc discharge method with bright PL in the violet-blue and blue-green region was re- ported by Bottini and co-workers [12]. Recently, boron- and nitrogen-doped CDs were synthesized by the arc discharge method from graphite using B_2H_6 for boron doping and NH_3 for nitrogen doping (Figure 1) [13].

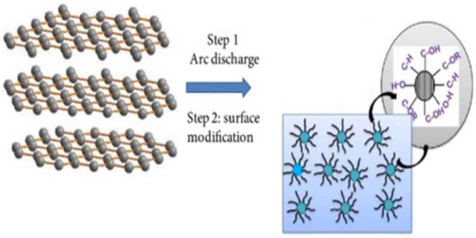

Figure 1. *Synthesis of CDs by an arc discharge method [13].*

2.1.2 Laser ablation method

The laser ablation technique has been widely used for making CDs, which are detached from larger molecular structures, in various sizes (Figure 2). Synthesis of CDs from graphite powder by using a laser ablation technique was first reported by Sun and co-workers in 2006 [9]. Upon laser excitation from a Nd:YAG (1064 nm, 10 Hz) source in an atmosphere of argon at 900°C and 75 kPa, CDs have been purposefully produced by hot-pressing a mixture of gra- phite powder and cement, followed by step- wise baking, curing, and annealing. Moreover, a single-step procedure that integrated syn- thesis and passivation was reported by Hu et al. using a pulsed Nd:YAG laser to irradiate graphite or carbon black dispersed in diamine hydrate, diethanolamine, or polyethylene glycol 2000 (PEG2000) under ultrasonication to aid in particle dispersal [14]. Recently, a laser irradiation technique from carbon glassy particles in the presence of PEG2000 has been employed for preparing photoluminescent CDs of around 3 nm size which are applied in bioimaging for cancer epithelial human cells [15].

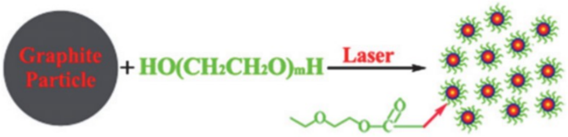

Figure 2. One-step synthesis of CDs in PEG2000 solvent [14].

2.1.3 Electrochemical oxidation method

Electrochemical procedure involves the use of a three-electrode cell containing working electrode, reference and counter electrode, as well as electrolyte. Carbon sources from larger molecular matter like carbon nanotube, graphite, and carbon fiber are used as electrodes in the presence of proper electrolytes under electrolytic processes of a pre-decided potential and number of cycles. Zhou and colleagues first reported synthesis of CDs from multiwalled carbon nanotubes in the presence of tetrabutylammonium perch- lorate as electrolyte [16]. Later, an electro -chemical method using graphite as electrode in the presence of phosphate buffer at neutral has been employed for preparing water soluble pure CDs, which were successfully applied as potential biosensor, was reported by Zheng and co-workers (Figure 3) [17]. Recently, an electrochemical technique for synthesis of CDs with polyaniline hybrid exhibited high QY and purity was reported. The as-prepared CDs-polyaniline composite showed high capacitance and was applied in energy-related devices [18].

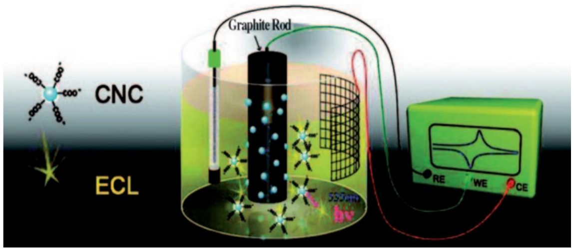

Figure 3. Electrochemical production of CDs from a graphite rod which are capable of electrochemilumi- nescence (ECL) [17].

2.1.4. Chemical oxidation method

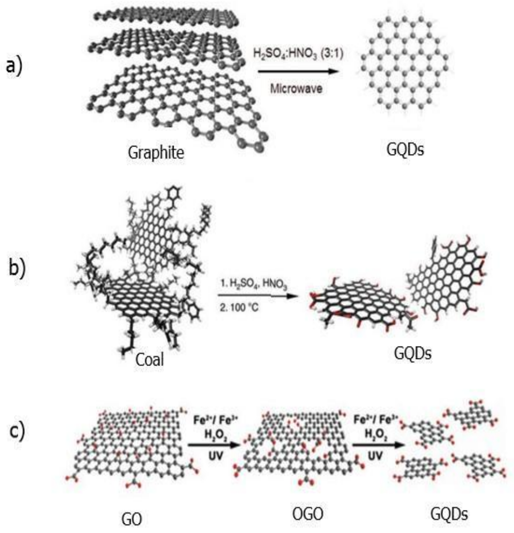

Figure 4. Electrochemical production of CDs by using graphite (a), coal (b), and GO (c) [19,21,25].

Oxidative cleavage is most frequently used for synthesis of CDs from larger graphitized carbon materials such as graphite [19], carbon black [20], coal [21], carbon fiber [22], graphene [23,24] or graphene oxide (GO) [25]. In this chemical oxidation process, strong acids are often used as the oxidants. The cheapest among all the precursors is coal. Coal can be more easily cleaved compared to graphite (Figure 4a) [19], because it contains nanosized graphitized carbon domains weakly linked by amorphous carbon (Figure 4b) [21]. In the original process, a mixture of highly concentrated nitric and sulfuric acids was used; however, the difficulty to remove sulfuric acid increases the synthesis cost. In addition, carbon black that is a cheap paracrystalline carbon can also be more easily cleaved by acids compared to graphite [20]. Therefore, coal and carbon black are more promising than others for large-scale industrial production using oxidative cleavage methods. Nonacid oxidants such as oxone [26] and H_2O_2 [27], which are free radical initiators, have also been used to exfoliate CDs (Figure 4c) [28]. These oxidants are less environmentally hazardous compared to strong acids. It is noteworthy that oxidatively exfoliated GQDs unavoidably bear abundant oxygenated groups, which are mainly -COOH, -OH, and C-O-C groups, and the induced oxygenated species and their ratio depend on the used oxidants.

2.2 Synthesis of carbon dots via "bottom-up" approach

The bottom-up approaches, on the other hand, synthesize CDs from molecular precursors for example citric acid, glucose, and other carbohydrates using thermal decomposition [29,30], hydrothermal or solvo -thermal treatment [31,32], microwave assisted method [33,34], and other routes [37-40]. Compared to the "top-down" approaches, the bottom-up approaches have obvious advantages in turning the composition and photo properties (such as high yields and quantum yields) by careful selection of precursors and carbonization conditions.

2.2.1 Thermal heating method

Previously, thermal decomposition has been employed for fabricating different semiconductor and magnetic nanomaterials. Recently, numerous studies have reported that external heat can contribute to the dehydration and carbonization of organic molecules and turn them into CDs. This method has advantages of facile, solvent free, wide precursor tolerance, economical and scalable production. For instance, Martidale and co-workers prepared inexpensive CQDs by straightforward thermolysis of citric acid in a simple one-pot, multigram process which is scalable [29]. Similarly, Chen et al. reported green synthesis of water-soluble CNDs with multicolor photoluminescence from poly- ethylene glycol by a simple one-pot thermal treatment [30]. In the formation of such CNDs, PEG played two essential roles that are the carbon source and surface passivating agent. The as-prepared CNDs have shown to be soluble in water and common organic solvents, and emitted bright multicolor fluorescence with excitation and pH dependent emission properties (Figure 5).

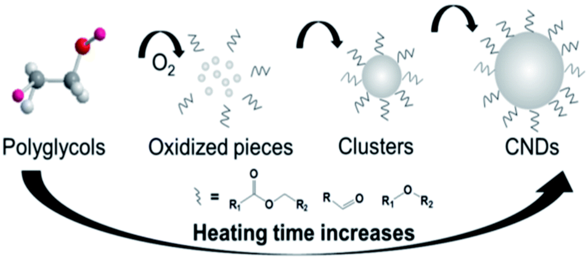

Figure 5. *Formation of NCDs via thermal decomposition method [30]*

2.2.2 Hydrothermal or solvothermal method

Hydrothermal carbonization is a facile, economical, and environmentally friendly route to produce novel carbon-based materials from saccharides, carbohydrates, organic acids, and natural materials. In general, a solution of organic precursor is sealed and reacted in a stainless steel autoclave reactor which is then heated to a designed temperature and kept for an intentional period of time.

A facile hydrothermal synthesis route of N and S, N co-doped graphene quantum dots (GQDs) were developed by Qu and colleagues which used citric acid as precursors and urea, thiourea as N andS dopants, respectively. Both N and S, N doped GQDs showed high quantum yield (78 % and 71 %), excitation independent under excitation of 340 – 400 nm and single exponential decay under UV excitation. Due to doping with sulfur, which alters the surface state of GQDs, a broad absorption band in the visible region appeared in S, N co-doped GQDs. Interestingly, S, N co-doped GQDs exhibited different color emission under excitation of 420 – 520 nm due to its absorption in the visible region [31].

Yuan et al. reported bright multicolor fluorescent CDs by simply controlling the fusion and carbonization of citric acid and diaminonaphthalene under solvothermal method at 200°C in a various time (Figure 6). The synthesized CDs exhibited multicolor emission of blue, green, yellow, orange, and red with the PLs were centered at 430, 513, 535, 565, and 604 nm, respectively [32].

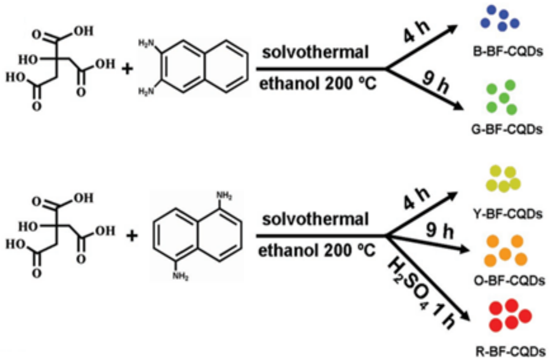

Figure 6. *Solvothermal synthetic route of multicolor emission CDs, which are blue, green, yellow, orange, and red from up to down, respectively [32]*

2.2.3 Microwave assisted method

Microwave, a type of electromagnetic radiation with a large wavelength range from 1 mm to 1m commonly used in daily life and scientific research, is capable of providing intensive energy to break off the chemical bonds of the precursors. Thus, the microwave-assisted method is considered an energy efficient approach for producing CDs. Moreover, the reaction time for synthesizing CDs by microwave assisted method may be extremely reduced. In general, microwave assisted methods include the pyrolysis and functionalization of the reactants.

A fast large-scale synthesis of fluorescent carbon dots (CDs) without high temperature or high pressure has been developed by Wang et al. [33]. Using benzene diols (catechol, resorcinol and hydroquinone) as the carbon precursor and sulfuric acid as the catalyst, three distinct CDs with strong and stable luminescence were prepared via a microwave -assisted method within 2 min (Figure 7).

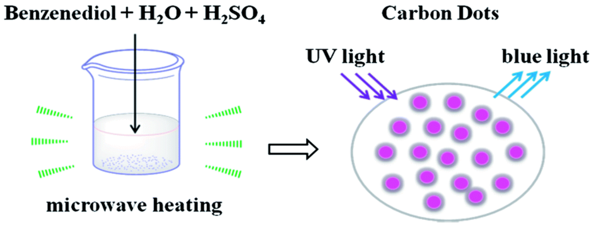

Figure 7. *Microwave assisted synthetic route of fluorescent CDs [33]*

Similarly, CDs can be prepared by microwave-assisted heating using a mixture of aqueous solution of citric acid with 2-ethylenediamine [34]. The as-prepared CDs showed excitation-dependent fluorescent spectra. The fluorescent properties of synthesized CDs due to the presence of carboxyl and amine groups are revealed by FTIR analyses.

2.2.4 Ultrasonic method

Some organic materials under ultrasonic irradiation will go through the process of dehydration, polymerization, and carbonization successively leading to the formation of nuclei. Thus, ultrasonic synthetic methods for preparing CDs are developed. For example, water-soluble fluorescent N-doped carbon dots (NCDs) were synthesized via a facile one-pot ultrasonic reaction between glucose and ammonium hydroxide by Ma and co-workers [35]. In this process, a suitable amount (2.0 g) of glucose was added to aqueous ammonia (30%, 40 mL) and deionized water (100 mL) to form an achromatic suspension which is then ultrasonic treated for 24 h at room temperature. In another report, ultrasonication of glucose along with acid or alkali yields water-soluble and spherical CDs. The as-prepared CDs exhibited NIR emission, one of the very important properties, which can be utilized in photothermal therapy of cancer [36].

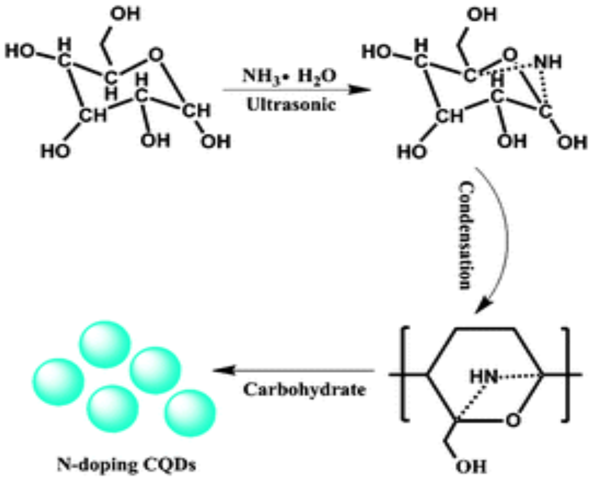

Figure 8. *The formation process of the NCDs [35]*

2.2.5 Other "bottom-up" methods

Li et al. reported a facile and versatile molten salt method to prepare hydrosoluble carbon dots from various precursors with high yield and large scale [37]. Citric acid and other precursors such as sodium lignosulphonate, sucrose, glucose, and *p*-phenylenediamine were used as a precursor in the eutectic mixture of $NaNO_3/KNO_3/NaNO_2$ (7:53:40 mass ratio) with a melting point of 140°C.

Chen et al. developed a process to synthesize carbon quantum dots (CQDs) on a large scale by using hydroquinone and ethylenediamine (EDA) as the precursors and the EDA-catalyzed decomposition of hydrogen peroxide at room temperature (Figure 9) [38].

Li et al. reported a simple, fast, energy and labor efficient for synthesizing CDs which involves only the mixing of a saccharide and base [39]. This process produced uniform and green luminescent carbon dots with an average size of 3.5 nm without the need for additional energy input or external heating.

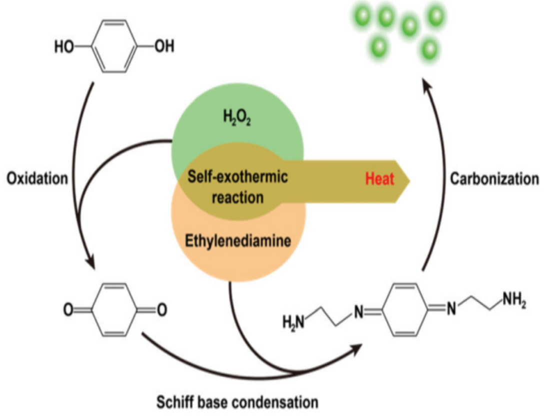

Figure 9. *Reaction process of core–shell structural CDs at room temperature [38]*

The electrochemical synthesis was also used for producing CDs. In this method, the electrochemical carbonization of low molecular-weight compounds (alcohols under basic conditions) and the size of the resultant CDs could be adjustable by changing the synthesis potential [40].

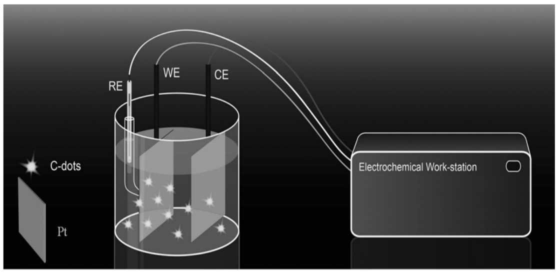

Figure 10. *Electrochemical carbonization of low- molecular-weight compounds for synthesis of CDs [40]*

3. PROPERTIES OF CARBON DOTS

3.1 Morphology and structure of CDs

CDs is the newest member in the family of carbon materials which are composed of both sp^2 and sp^3 hybrid carbon networks [41]. Moreover, they contain or can be easily functionalized with functional groups (hydroxyl, carboxyl, carbonyl, amino, and epoxy) over their surfaces. Therefore, they offer extra advantages for binding with both inorganic and organic moieties enhancing their properties and applications [42]. Surface functionalization has a significant impact on the PL properties and, moreover, is the precondition for the further application of CDs [43].

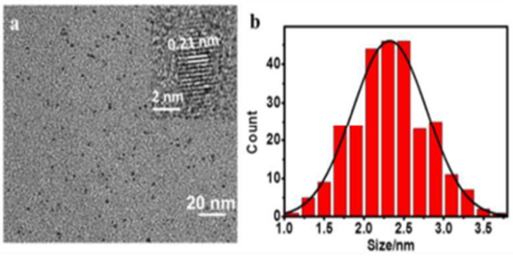

Figure 11. *(a) TEM image of the CDs (insert is the HRTEM image of one nanoparticle); and (b) the size distribution of CDs [37]*

Transmission electron microscopy (TEM) has been a primary technique for visualization of CDs, providing important information upon particle morphology, size distribution, and crystalline organization. High-resolution TEM (HRTEM) experiments have been applied to confirm the periodicity of the graphitic core, reflecting its crystalline nature. For carbon dots, the corresponding structure could be crystalline, amorphous or crystalline with partly amorphous. Figure 11. presents a TEM and HRTEM image of an example CDs. The TEM demonstrated that CDs are well-dispersed and have a narrow size distribution with an average size of around 2.4 nm. The HRTEM showed that the lattice spacing of CDs is 0.21 nm, which corresponds to the (100) facet of graphitic carbon [37].

3.2 Composition of carbon dots

Generally, luminescent CDs are composed of a carbon core and surface functional groups binding to the surface of the CDs. The basic elements of luminescent CDs are C, H, and O in the form of carbon core, carboxyl groups and hydroxyl groups which are attached on the surface of the CDs. In addition, there are some doping element such as B [46], P [47], S [48], and especially N [32, 35], the most popular doping element in CDs that introduced N atom to carbon lattice or functional groups such as NH_2, CONH, or NOx to the surface of the CDs. There are also publications on synthesis of co-doping CDs, for instant N, S co-doped CDs [31]. Recently, doping CDs with metal elements such as Cu [49], Zn [50] or Se [51] are also reported. Previous reports have shown that the emission properties of the CDs could be modulated by functionalization of the CDs with various types of organic molecules or solvents.

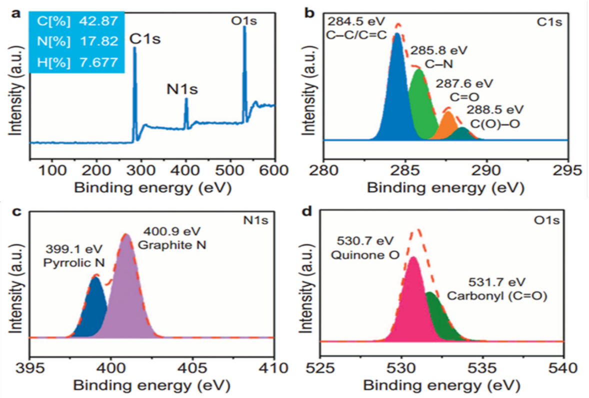

Figure 12. *(a-d) XPS (full survey, C1s, N1s, and O1s, respectively) of N-GQDs (insets of (a) is the element amount from element analysis) [52]*

Elucidating the functional groups upon CDs' surfaces is accomplished through application of several widely used analytical methods. X-ray photoelectron spectroscopy (XPS) provides information upon specific atomic units present upon CDs' surface. An example of an XPS analysis is provided in Figure 12 [52]. The spectral analysis reveals the distinct nitrogen-, oxygen-, and carbon-bonded units displayed upon the CDs' surface. Fourier transform infrared (FTIR) spectroscopy usually complements XPS, illuminating distinct functional units through recording of typical vibration bands (Figure 13) [53].

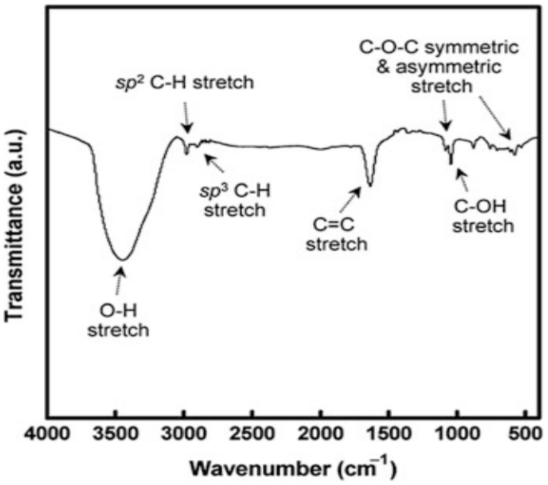

Figure 13. *FTIR spectrum of a CDs sample (distinct vibration bands corresponding to CDs' surface units are indicated) [53]*

3.3 Optical properties of carbon dots

3.3.1 Absorbance

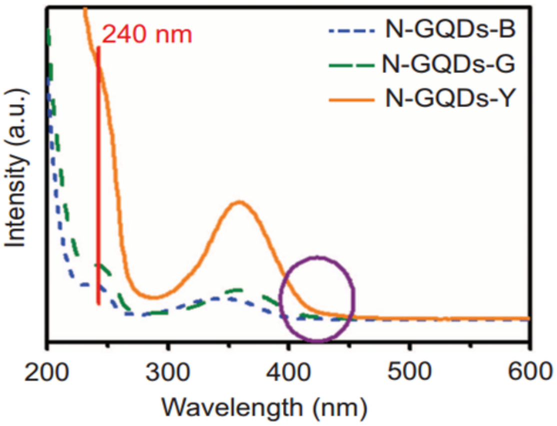

Figure 14. *UV-vis spectra of CDs sample [28]*

According to previous reports, CDs are effective in photon-harvesting in short-wavelength region because of π-π^* transition of C=C bonds, thus they typically show strong optical absorption in the UV region (260–320 nm), with a tail extending into the visible range [4, 53]. The positions of the UV absorption peaks of CDs prepared by different methods are quite different. In the case of longer wavelength color emission or multicolor emission CDs, the absorption profiles of them may demonstrate multiple electronic absorption transitions and could be assigned to π-π^* transition of C=C bonds from the aromatic sp^2 domains and (n-π^*) transition of functional groups C-O/C=O and the transition of conjugated C-N/C=N [52].

3.3.2 Photoluminescence (PL)

CDs with different color from blue to red have been synthesized and most common are blue and green, which in many cases show wide emission spectra due to the heteto-geneity in chemical composition and size.

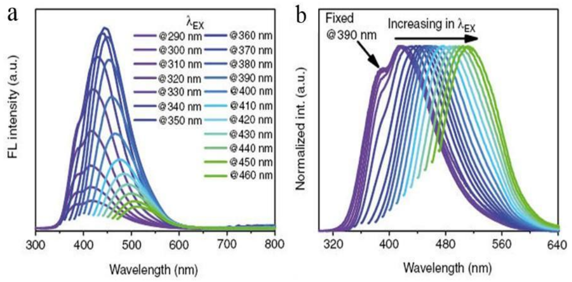

Figure 15. *(a, b) PL and normalized PL spectra of a CDs sample [12]*

Frequently, the PL intensity maximum of CDs red-shifts as the excitation wavelength increases exhibiting excitation dependent emission wavelength and intensity [55]. As shown in Figure 15, the PL spectra of nitrogen -doped CDs show excitation shifts by changing the excitation wavelength from 290 to 460 nm, along with a notable change of the PL intensities [12]. CDs have only one maximum emission which is excited by the only maximum excitation. The excitation-independent fluorescence behavior has also emerged, which may be attributed to their uniform size and surface chemistry [56], and the intensity of fluorescence increased to the maximum and then decreased (Figure 15) [12]. In general, the PL emission spectra of CDs are symmetrical in the main, with large Stokes shifts as compared with that of organic dyes [57]. In addition, previous reports have shown that by adjusting the synthetic routes, CDs which exhibited PL in the visible-to-near infrared (NIR) spectral range can also be achieved [35]. The NIR PL emission is particularly useful that makes CDs suitable for the imaging of biological samples with deeper depths in the NIR window. Moreover, PL from CDs can also be quenched by electron acceptors or donors. The photo-induced electron transfer properties of CDs made them promising materials for applications in energy conversion.

3.3.3 Quantum yields (QY)

Quantum yield (QY) is a significant parameter to characterize PL. The quantum yield (QY) of bare CDs is usually very low (typically <10%) due to the emissive traps on the surface. To increase the QY, a number of methods have been developed, such as passivation [58], doping with other elements [59], and purification processes. Sun et al. functionalized CDs with diamine -terminated oligomeric PEG (PEG_{1500N}) or poly(pro pi-onyl - ethyleneimine - co - ethylene-imine)(PPEI -EI) to obtain the products which yielded bright emissions (4–10%) [9], for example. Another route that Zheng proposed by Zheng is a reductive pathway to promote the QY from 2% to 24% via treating the CDs with $NaBH_4$ [60]. In addition, Qu et al. fabricated N doped CDs exhibiting almost the highest QY of 94% [61].

3.3.4 Fluorescent mechanisms

Up to now, many groups have proposed various mechanisms to uncover the fluorescent origin of CDs, which may guide tuning the performance of the CDs. In Pan's opinion, the fluorescence is assigned to the free zigzag sites with a carbine-like triplet ground stage [24]. Afterwards, Zhu et al. hypothesized that the coexistence of defect state emission and intrinsic state emission and their competitive emission centers lead to green and blue emission, explaining most of the fluorescent features [62]. Another hypothesis made by Liu et al. assumed that the π-π electron transition contributes to the fluorescence and strong electron donating effect of functional groups can boost the charge transfer efficiency [63]. Moreover, the size of CDs is also thought to be the possible reasons for the excitation-dependent phenomenon that fluorescent emissions can red-shift as the increase of the excitation wavelength [64]. Hu et al. synthesized a series of CDs by changing the reagents and reaction conditions and proposed that the surface epoxides or hydroxyls were predominantly responsible for the resulting PL red shift [65]. More recently, Ding et al. also hypothesized that red shift of the emission peaks of CDs, changing from 440 to 625 nm, was attributed to a gradual reduction of band-gap with increasing incorporation of oxygen species into the surface functional groups [66]. However, after years of intensive research, the exact mechanism for the PL of carbon dots is still under debate.

4. APPLICATIONS OF CARBON DOTS IN CHEMICAL SENSING

The most essential property of CDs is that they exhibited excellent optical performance compared with that of other carbon nanomaterials. Extensive studies have been devoted to developing the optical applications of CDs, especially fluorescence - based applications. As novel fluorescent probes, CDs are providing great potential for sensing applications because they are highly sensitive to analytes in a very short time. In addition, the ultras mall size, high photostability, low toxicity, good bio-compatibility and excellent dispersion of CDs result in improved detection sensitivity, stability, selectivity and security compared with traditional organic dyes and semiconductor quantum dots. Up to now, the detection of analytes include inorganic metal cations [32, 67-74], non-metallic anions [75-77] and small organic molecules [46, 78-83] based on either fluorescence turn-on or turn-off mechanisms. The following of this chapter will focus on recent fluorescence sensing applications of CDs.

4.1 Detection of inorganic ions

CDs have been widely used as fluorescence sensing probes for detection of inorganic ions including metal cations [32, 67-74] and non-metallic anions [75-77].

Though metal cations play important roles in environmental, biological and chemical systems, they also pose toxicity to human beings because of the possible leading to serious damage of the kidneys, liver and brain. Therefore, highly sensitive and selective probes for metal cations are highly desired. Since CDs display strong PL and possess rich organic functional groups on their surfaces, they are considered suitable for fluorescence sensing probes for metal ions detection. To these days, numerous metal cations including Fe^{3+} [32], Ag^{+} [67], Au^{3+} [68], Hg^{2+} [69], Cu^{2+} [70], Cr^{6+} [71], Cd^{2+} [72], Pb^{2+} [73], and Ni^{2+} [74], have been detected using different CD-based fluorescent sensors. Most studies mainly focused on the detection of Fe^{3+}, Hg^{2+} and Cu^{2+}, probably because of their prominent role or high toxicity in biological systems.

Recently, CDs have also been employed as fluorescent probes to detect non-metallic ions including sulfide ions [75] pyrophosphate (PPi) ions [76], and sulphite [77] via “on– off–on” fluorescence responses.

4.2 Detection of small organic molecules

Similar to the selective and sensitive detection of inorganic ions, monitoring small organic molecules with fluorescent CDs has also become an attractive topic in recent years. Organic materials such as glucose [46], ascorbic acid [78], bisphenol A [79], dihydroxybenzene [80], hydroquinone [81], 2,4,6-trinitrotoluene [82], and 2,4,6-trinitrophenol (TNP) [83] have been optically detected using fluorescent CDs probes based on a turn-on or turn-off fluorescence response. The fluorescence of CDs can be quenched directly by the detected organic molecules with the aid of metal ions or oxidation agents. Another mechanism is that the fluorescence of CDs, as an indirect sensing probe, can first be quenched by metal ions and then recovered by specific organic molecules.

4.3 Fluorescence sensing mechanism

The above mentioned has shown that CDs could be effectively applied as fluorescent probes for selective and sensitive detections of inorganic ions and small organic molecules. Although there are various targets, the constructed fluorescence sensing platform was primarily based on turn-off (fluorescence quenching) and turn-on (fluorescence recovering) fluorescence responses. On one hand, the turn-off response based on the fluorescence quenching of CDs or functionalized CDs by targets appears to be static quenching (complexation) [70], dynamic quenching (collisional deactivation) [84] or sometimes involving both static and dynamic quenching mechanisms, which frequently can be analyzed using the evaluation of fluorescence lifetime. The turn-on fluorescence response, on the other hand, based on the mechanism which is usually considered to contain two steps [80]. Firstly, the fluorescence quenching of CDs or functionalized CDs occurs because of the strong interaction between CDs (or functionalized CDs) and quencher. Secondly, the preformed composite structure of CDs and quencher is broken down with the addition of targets, leading to the freedom of fluorescent CDs into solution; therefore, the corres- ponding fluorescence is recovered. Never- theless, the fluorescence recovering process is still ambiguous when CDs, quencher and target are in coexistence.

5. CONCLUSION AND OUTLOOK

To sum up, recent progress of CDs in terms of their rational synthesis, properties and sensing applications are reviewed. Numerous synthetic methodologies of CDs are being reported every year; however, simple and high yield routes in large scale still remain a challenge for scientists. Despite a large number of publications, the photophysical properties of CDs are not yet theoretical explanations clearly and still that leave a bright scope of research for the physicists and physical chemists in the near future. Due to its outstanding physical and chemical properties, CDs are providing great potential for sensing applications. Moreover, because of their biocompatibility, CDs are expected to replace semiconductor quantum dots and will find a wide range of applications in bioimaging and biosensors. However, to explore environmentally friendly, economical and facile processes for synthesis of highly PL emission CDs, especially longer wavelength color emission CDs and their photolumi- nescence mechanism are still highly desired.

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