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Review Article

Preparation and Application of Fluorescent Carbon Dots

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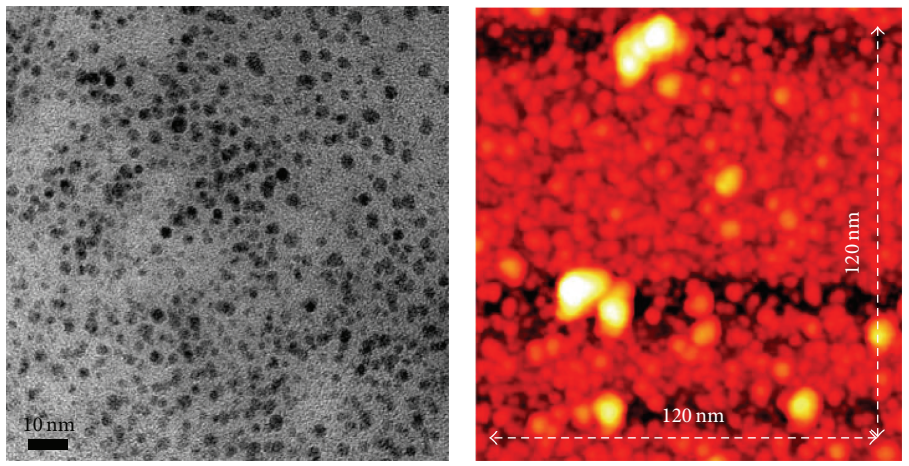
Fluorescent carbon dots (CDs) are a novel type of fluorescent nanomaterials, which not only possess the specific quantum confinement effects of nanomaterials due to the small size of nanomaterials, but also have good biocompatibility and high fluorescence. Meanwhile, fluorescence CDs overcome the shortcomings of high toxicity of traditional nanomaterials. Moreover, the preparation procedure of fluorescent CDs is simple and easy. Therefore, fluorescent CDs have great potential applied in photocatalysis, biochemical sensing, bioimaging, drug delivery, and other related areas. In this paper, recent hot researches on fluorescent CDs are reviewed and some problems in the progress of fluorescent CDs are also summarized. At last, a future outlook in this direction is presented.

1. Introduction

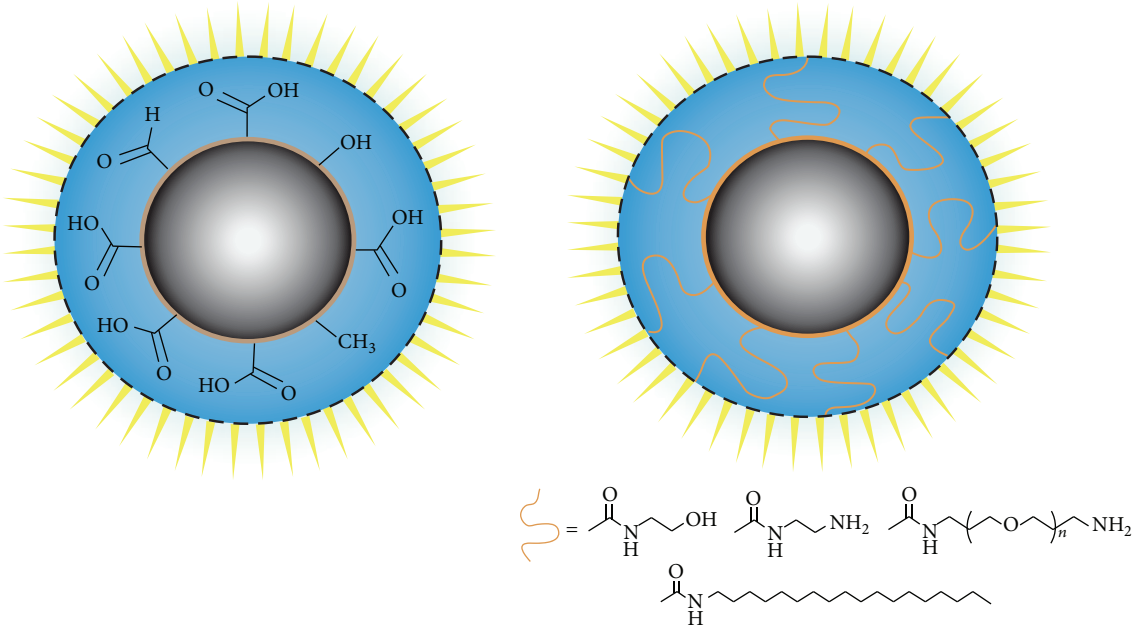
Nanotechnology is one of the most important technologies in 21st century. Currently, nanotechnology has been widely applied in numerous fields, such as biomedical and chemical analysis. In recent years, fluorescent nanomaterials have garnered much interest as potential competitors to traditional fluorescent dye probe and developed quite rapidly due to the extensive demand of fluorescent probe in chemical sensing, biological monitoring, and other related fields. Compared with the traditional fluorescent dye, fluorescent nanomaterials have quantum size effect and the unique effects of nanomaterials, which can overcome many shortcomings of the latter, such as the low stability, weak fluorescence intensity, and fast photobleaching. Therefore, fluorescent nanomaterials have been applied widely in the physical, biological, and chemistry as well as other related fields [1]. Among many kinds of nanoparticles, semiconductor quantum dots have become the focus of attention due to their unique electronic and luminescent properties [2–4]. However, semiconductor quantum dots usually contain heavy metals, which are general great toxic and limit their further applications in the field of biomedicine [5–7]. Thereby, the development of new nontoxic heavy metal-contained nanomaterials is one of the current trends.

In 2004, Xu et al. [8] discovered accidentally this kind of carbon nanoparticles with fluorescent properties for the first time when they separated single-walled carbon nanotubes using gel electrophoresis from carbon soot produced by arc discharge. Based on this study, in 2006, Sun et al. [9] synthesised fluorescent carbon nanoparticles with diameter less than 10 nm and named them carbon dots (CDs). The discovery of CDs has gathered to widespread concern of scientific researchers; in particular, their low toxicity and stable chemical properties make them become powerful candidates for new types of fluorescent probe and overcome the common drawbacks of previous fluorescent probes. In addition, fluorescent CDs possess rather strong ability to bind with other organic and inorganic molecules due to their abundant surface groups, so that fluorescent CDs can be manipulated via a series of controllable chemical treatments and satisfied the demands in the photocatalytic, biochemical, and chemical sensing, bioimaging, and drug carrier. Currently, the researches of fluorescent CDs mainly focus on two aspects; one is developing rapid, simple preparation method of fluorescent CDs, and the other is expanding the application field. This paper reviews the recent progress in these two aspects and especially discusses the advantages of fluorescent CDs applied in these new scientific fields.



(a) (b)

Figure 1: (a) HR-TEM image, (b) AFM image (reproduced with permission from [11]).



(a) (b)

Figure 2: Depiction of Cdots (a) after surface oxidation treatment and (b) after functionalization with surface passivation reagents (reproduced with permission from [12]).

2. Structures and Properties of CDs

Generally, CDs are nearly spherical nanocrystals with the diameter less than 10 nm and comprising few molecules or atoms of nanoclusters (Figure 1) [10, 11]. Compared with those larger particles like quantum dots, the size of carbon particles is generally only a few nanometers, and molecular weight is also only a few thousand to tens of thousands. Generally, there exist a large amount of -OH and -COOH and $-NH_2$ and other groups on CDs surfaces (Figure 2) [9], which endow CDs with good water solubility and polymerization ability with various inorganic, organic, or biologically active substances.

2.1. The Optical Properties of CDs. CDs have strong absorption in the ultraviolet region, which can also extend to visible region [12]. After modification of some passivating agents, the absorption spectral region may be red shift continuously [13]. The luminescence properties of CDs are mainly the photoluminescence and electrochemical luminescence, in which photoluminescence is the most prominent

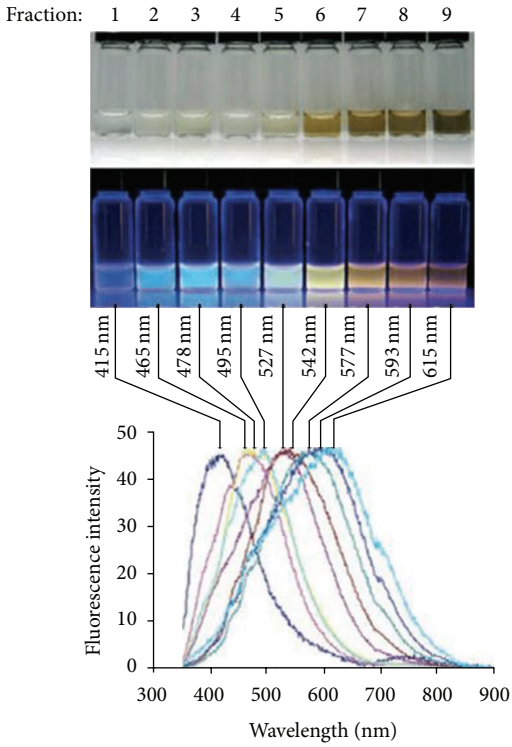


Figure 3: Optical characterization of the purified CNPs. Optical images illuminated under white (top) and UV light (312 nm, center). Bottom: fluorescence emission spectra (excitation at 315 nm) of the corresponding CNP solutions. The maximum emission wavelengths are indicated above the spectra (reproduced with permission from [14]).

performance. As an important role in almost all areas of fluorescent nanomaterials, the excellent optical properties of CDs mainly include high fluorescence stability, nonblinking, tunable excitation, and emission wavelengths (Figure 3) [14–17]. However, the emitting mechanisms of CDs are still not clear, only keeping the phenomenon levels. The in-depth quantum interpretation needs to be established. Some researchers speculated that the emitting mechanisms of CDs involve quantum confinement effect, stabilizing surface trap, or exciton recombination radiation [18].

2.2. Biocompatibility and Low Toxicity of CDs. Since carbon element is the skeleton of all living body, full carbon nanomaterials have a lower toxicity compared with other nanomaterials; simultaneously, the particle size of CDs is smaller and then more convenient to enter the cell in vivo, which makes CDs have great potential application in the biological fields. In addition, the surface of CDs contains a lot of functional groups, so that the surface of CDs can be modified with organic, inorganic, polymer, and other substances endowing different functional properties.

3. Preparation of CDs

In recent decade, there is great progress in the preparation process of CDs, not only simplifying the manufacturing process, but also optimizing the luminescence properties of the CDs. Basically, self-preparation processes from the bottom-up and the top-down approaches are two main categories. Since the top-down approach is through cutting, oxidation, the larger carbon cluster structure is cleaved into small carbon nanoparticles resulting in CDs with smaller particle diameter. On the contrary, the bottom-up approach is based on series of chemical reactions of small molecule precursors to form nanoscale CDs.

3.1. Top-Down Approach. Top-down preparations of fluorescence CDs are the early preparation approaches, including arc-discharge method [8, 19], electrochemical oxidation [20–23], and laser ablation [24, 25]. In 2004, Xu et al. [8] firstly separated accidentally fluorescent nanoparticle from the products when they prepared the single-walled carbon nanotubes by arc discharge. They also introduced nitryl onto the fluorescent CDs by arc discharging fuming nitric acid, improving the hydrophilicity of nanomaterials. After that, NaOH solution (pH = 8.4) was used to extract the precipitate to give a black suspension and obtained three groups of fluorescent carbon nanoparticles with different molecular weights after further electrophoretic separation. These three groups of fluorescent carbon nanoparticles emit blue green, yellow, and orange fluorescence, respectively, wherein the fluorescence quantum yield of yellow phosphor carbon nanomaterials can reach 1.6%. Subsequently, Sun et al. pioneered in synthesis of fluorescent CDs by means of laser ablation [26].

Zhou and his coworkers [22] used electrochemical methods for preparing fluorescent CDs. They used multiwalled carbon nanotubes as the working electrode grown in carbon membrane by means of chemical vapor deposition (CVD) method and the cycle voltage to obtain the CDs with blue fluorescence. The particle size of CDs produced in their method is 2.8 nm, and the fluorescence quantum yield is about 6.4%. Subsequently, some research group obtained CDs by means of the same method only replacing the solution with aqueous solution and electrochemical oxidation of graphite rods shock. The fluorescence quantum yield is about 1.2% [20, 23]. In order to further improve the efficiency of the electrochemical method for preparing CDs, the researchers prepared the fluorescent CDs by using ionic liquid assisted electrochemical exfoliation of graphite electrodes. Using the ionic liquid solvent to replace the traditional solution can play a dual role of dissolving and catalysis, in which the reaction rate can be improved several times. Furthermore, by adjusting the ratio of the ionic liquid and water, the fluorescence emission wavelengths of CDs can be adjusted [21]. However, the fluorescence quantum yield of the CDs prepared in electrochemical methods is not high and needs further improvement.

Compared with the multistep preparation method of CDs, one-step reaction processes not only simplify the preparation procedure and the prepared CDs also with better fluorescent properties, but also can obtain CDs with different fluorescent properties by choosing different organic reaction solution. For example, Hu et al. [27] combined laser ablation

and surface passivation merger in one-step reaction, with the polyethylene solution under laser radiation for 4 h, to get a black suspension. After separating the black suspension, they obtained fluorescence CDs with particle size about 3.2 nm, and the quantum yield is 12.2%, which significantly improved the fluorescence quantum yield of CDs.

3.2. Bottom-Up Approach. Bottom-up approaches are based on the polymerization reaction for small molecules to the formation of nanoscale CDs. This strategy includes hydrothermal method [14, 28–33], microwave-assisted pyrolysis method [34–38], ultrasonic method [39], acid dehydration method [40], and pyrolysis method [41, 42]. Among them, the most widely used are the hydrothermal method and microwave-assisted pyrolysis method, which can be realized by the one-step method for preparing fluorescent CDs.

In 2007, Liu and coworkers [14] first prepared CDs by hydrothermal methods. They mixed candle ash as the carbon source with nitric acid through heat reflux and generated a black homogeneous solution and then purified through a series of centrifugation, dialysis, gel electrophoresis, and other processes to obtain fluorescent CDs with different particle sizes. They found that the emission wavelengths of fluorescent CDs depend on the particle sizes even under the same excitation light (λ_{ex}, 315 nm); the emission wavelength is gradually red shift with the increasing of the particle size, which reflects fully an optical character of fluorescent CDs, named elementary excitations and multiemission. In the past two years, a lot of reports are about the researches of preparing CDs through hydrothermal method using different carbon sources, and the fluorescence quantum yield of CDs has been greatly increased. For instance, Gao and so forth [32] chose C60 as the carbon source and CTAB as passivator to prepared CDs with high fluorescence quantum yield up to 60%. Even more, the fluorescent CDs prepared in their method possess the distinctive property of aggregation induced enhanced emission, which is different from the common reports in the literatures.

Zhu et al. [35] developed a simple microwave method to synthesize the new type of CDs. With carbohydrate as a carbon source and PEG200 as both solvent and coating agent, the reaction system gradually changed from colorless to dark brown solution when under 500 W microwave power radiation for 2~10 min, and the product was diluted with water to obtain fluorescent CDs. In this method, the particle size and the quantum yields of fluorescent CDs depended on the reaction time. Wang et al. [36] created a "green," "fast," "economy" CDs synthesis method by means of microwave method. They first burn eggshell into ashes, then mixed the ashes with NaOH aqueous solution, and treated the solution via microwave radiation for five minutes to get CDs. This method is quite simple; the raw materials are cheap and available, and the consuming time is very short; the fluorescence quantum yield of CDs reaches to 14%. Chandra et al. [37] used sucrose as a carbon source and promote the synthesis of fluorescent CDs in phosphoric acid environment by microwave radiation. The reaction time is just 3 minutes and 40 seconds, and the prepared CDs are shining bright green fluorescence. Yang et al. [38] created a rapid synthesis method of amino modified CDs using chitosan as a carbon source under mild conditions and applied them to human lung adenocarcinoma A549 cells imaging.

4. Fluorescent Applications Carbon Dots

4.1. Photocatalysis. With the rising demand for low-carbon society, how to utilize full advantage of solar energy and other clean energies becomes an important issue. The appearance of photocatalytic technology caused the research of photocatalytic technology boom, involving solar energy, photovoltaic cells, self-cleaning materials, and environmental pollution control and many other related fields. However, the traditional photocatalytic materials such as TiO_2 and ZnO generally with absorption range in ultraviolet light, visible light cannot be taken as full advantage and have been greatly restricted in practical applications. Thus preparing nanomaterials with high stability and high visible light composite catalyst activity is of great significance in solving environmental problems and energy issues.

Cao et al. [43] prepared CDs through acid reflux dehydration method and modified the CDs with PEG1500, to obtain the CDs with surface coated metal gold or platinum cluster coated via liquid phase method. In this reaction system, the CDs play the role of electron donor and can restore gold salts or platinum salts ($HAuCl_4$ or H_2PtCl_6), so that the corresponding sites of metal on the CDs surface form CDs/Au composite. The gold-coated CDs were placed in a wide room with abundant carbon dioxide pass and kept at room temperature until they reach saturation. With visible light (425–720 nm) irradiation for five hours, the carbon dioxide can be restored to formic acid. Meanwhile, gold-coated or platinum-coated CDs can be used in the reduced reaction of water to give hydrogen.

Zhang et al. [44] prepared CDs by electrochemical method, in which the CH_3COOAg and PVP were dissolved in prepared CDs solution, and dropping Na_2HPO_4 solution to prepared CDs/Ag_3SO_4 composite catalyst. Meanwhile, CH_3COOAg and PVP were dissolved in prepared CDs solution in sunlight reflux with dropping Na_2HPO_4 solution to obtain CDs/Ag/Ag_3SO_4 composite catalyst. Both these two catalysts were used in the degradation reactions of methylene blue under visible light radiation. Their experimental results showed that the photocatalytic ability of CDs/Ag/Ag_3SO_4 is 5.5 times larger than that of CDs/Ag_3SO_4. In addition, the structure of CDs/Ag/Ag_3SO_4 is more stable in the catalytic process; when repeating the photocatalytic experiments, the catalytic efficiency has almost no change.

As one of the most common photocatalysts, TiO_2 has been widely used in the decomposition of organic pollution and H_2O to generate H_2 [45]. However, due to the quite large gap between the conduction band and the energy band of TiO_2, TiO_2 has only absorbed peak in very short wavelength ultraviolet. Thus visible light is the useless energy for TiO_2. In order to improve the photocatalytic properties of TiO_2, the researchers have done a lot of efforts and found that the composite of TiO_2 nanoparticles and carbon dots can

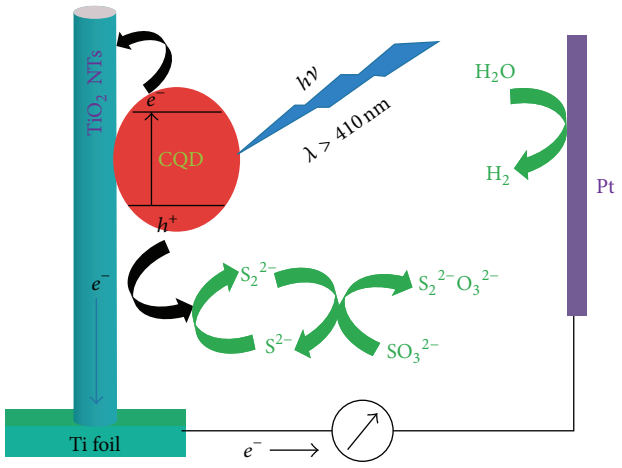


FIGURE 4: Illustration of the sensitization mechanism of CQDs (reproduced with permission from [46]).

effectively broaden the range of the optical response of the composite structure and increase the utilization of solar energy and transformation. For instance, Zhang et al. [46] used CDs-TiO_2 composites as catalyst successfully to get H_2 (Figure 4) from the water decomposition under visible light irradiation, wherein the introduction of CDs obviously broadens the light response range of TiO_2. Subsequently, based on the upconversion property of the CDs and the synergistic effect between the CdSe quantum dots and CDs, the CdSe quantum dots were served to modify the TiO_2-CQD nanocomposites, and the photocatalytic efficiency was greatly improved [47]. Although photocatalytic technology still stays in the laboratory level and it is difficult to spread into everyday life, the photocatalytic technology as a new pollution control technology is huge potential in the utilization of new means of solar energy and is promising in future exploring.

4.2. Luminescent Device

4.2.1. LED Device. Guo et al. [48] synthesized a series of multicolor CDs by the thermolysis of epoxy group containing polystyrene microspheres (Figure 5). CDs produced under 200, 300, and 400°C could emit blue, orange, and white fluorescence with the excitation of single wavelength ultraviolet, respectively, and the fluorescent quantum yield is 47%. With the excellent properties, those CDs could be used as the above-mentioned three color LED devices. Wang et al. [49] used citric acid as carbon source to synthesize new CDs in octadecene coupled with 1-cetylamine as surface passivator. The max quantum yield of these CDs made white light emitting devices reach 0.083% under the irritation of 5 Ma/cm^2 ampere density.

4.2.2. Macrostructure Material. Zhang et al. [50] used electrochemistry corrosion of graphite electrode to produce the new types of CDs. Upon the addition of CDs on glass surface with the concentration of 1.3 mg/mL, the CDs thin film was obtained after being dried. The oxygen contained group at the CDs surface determined its sensitivity of humidity and the conductivity of CDs was in direct proportion to the relative humidity. Because of the high specific surface area and excellent stability of the CDs thin film, it is suitable for gas sensing.

Fan et al. [51] employed electrodeposition to prepare CDs by electrolyzing of graphite rods in SiO_2 nanosphere matrix. After dissolving the nanosphere matrix by HF, two-dimensional and three-dimensional mesh structure CDs were obtained (Figure 6). This unique structure has high absorbability for particular application. The nano-Au contained mesh structure of CDs could be used as probes for high sensitivity detection. Furthermore, the surface Raman scattering of nano-Au contained mesh structure CDs can gain 8 to 11 times of signal intensity comparing with the widely used SERS materials.

4.3. Chemical Sensing. Fluorescent carbon dots, due to their excellent optical properties, chemical stability, and good solubility in water, in the field of chemical sensing under great attention, are widely used in metal ion detection, anion detection, small organic molecules, and biomolecules detection. Like the semiconductor quantum dots, CDs by the interaction with the analyte can change the efficiency of recombination between the surfaces of the electron-hole pairs, which occurred in the fluorescence enhancement and quenching treatment to achieve quantitative or qualitative analysis of the measured object.

4.3.1. Metal Ion Probe. Carbon dots as a new fluorescent probe in solution are easily quenched efficiently by electron acceptor and thus can effectively detect metal ions in solution and determine the concentration of metal ions in a certain concentration range, to achieve the trace analysis of metal ions.

Hg^{2+} is one of the most toxic heavy metal ions in environment, has received the attention of scientific researchers. Currently, based on CDs as sensor, scientists have developed a variety of methods to detect Hg^{2+} [52–55]. Lu et al. [52] prepared a new type of CDs from grapefruit peel through hydrothermal method. As the Hg^{2+} can effectively quench the fluorescence of CDs, a new method for the detection of Hg^{2+} was developed, the detection limit of 0.23 nM, and this method has been successfully applied to the detection of Hg^{2+} in the river. Liu et al. [53] obtained CDs with excellent fluorescent stability by the polyethylene glycol (PEG) refluxed with NaOH; taking these CDs as a sensor can specifically detect Hg^{2+} in solution and the detection limit reaches 1 fM (Figures 7 and 8). This test method successfully detected Hg^{2+} in the rivers, lakes, and tap water samples and the sensitivity is very high. Zhang and Chen [54] used vitamin B as carbon and nitrogen sources and prepared a high fluorescence yield and nitrogen-rich fluorescence CDs by hydrothermal method. It was found that Hg^{2+} can be able to bind specifically with these CDs, the use of this fluorescent probe to establish a new method for label-free detection of Hg^{2+}, the detection limit of 0.23 nM. In addition to the detection of Hg^{2+}, scientists have

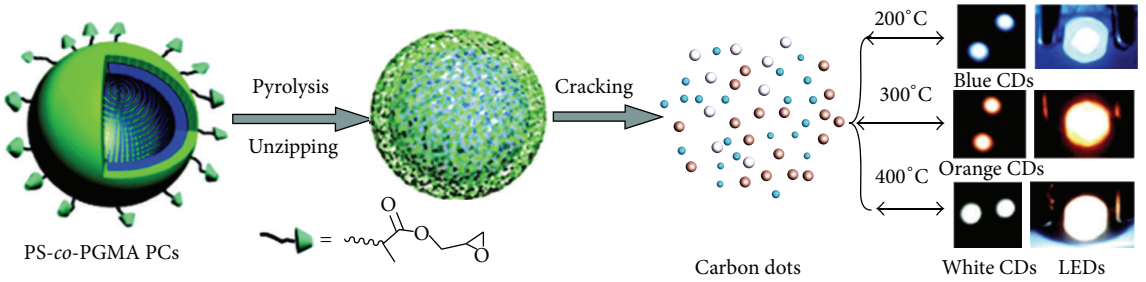


Figure 5: Schematic representation of the formation of carbon dots from the pyrolysis of photonic crystals (reproduced with permission from [48]).

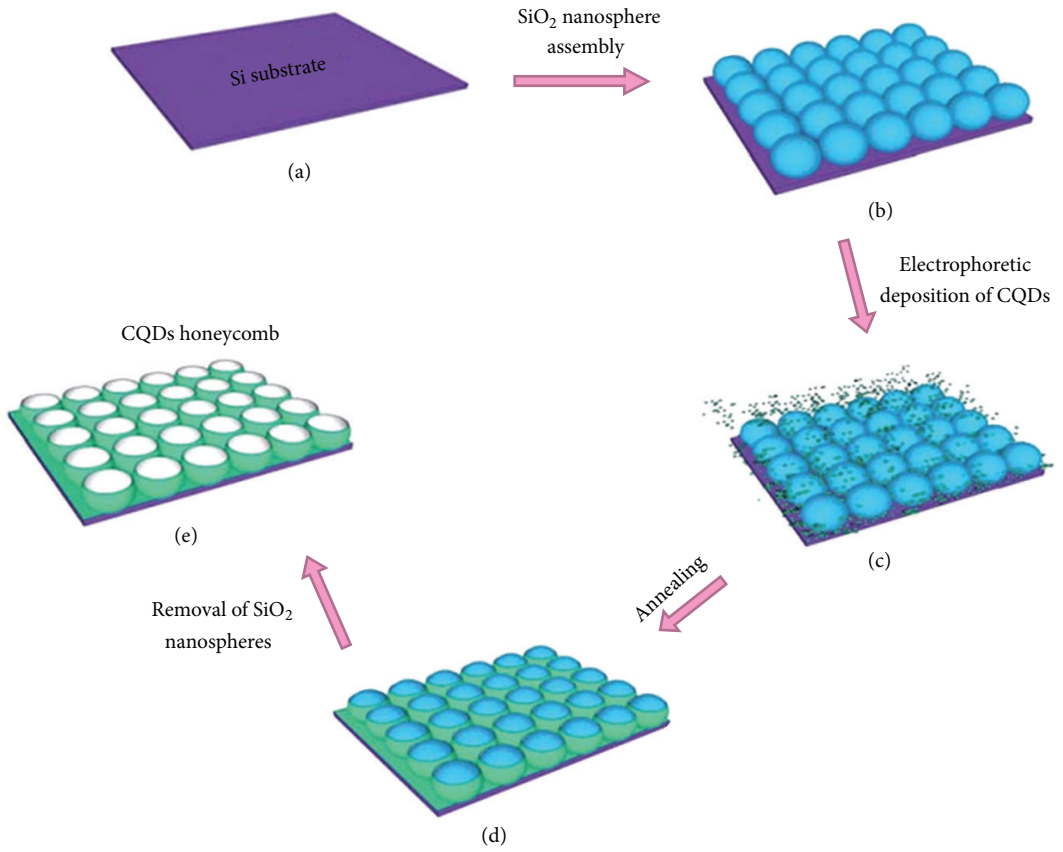


Figure 6: A scheme of the fabrication process for the formation of a 2D honeycomb structure of CDs (reproduced with permission from [51]).

also developed a variety of methods to detect Cu^{2+} [56, 57], Fe^{3+} [58, 59], Pb^{2+} [60], and Ag^{+} [61]. Because of the rich type of carbon sources, scientists will synthesize more excellent properties of CDs for the detection of heavy metal ions in environment.

4.3.2. Anions and Small Molecule Detection. During the metal ion sensor development, scientists expand the CDs probe used in detection of anions and small molecular. Unlike heavy metal ions detected fluorescence quenching mechanism CDs, anionic or small molecules generally by restoring fluorescence of the quenched CDs to achieve the purpose of detection.

Zong et al. [42] selected spherical mesoporous silica as nanoreactor, added to the solution of citric acid and three other inorganic salts (NaCl, LiCl, and KNO_3) and ultrasound to obtain CDs. The study found that the CDs can bond with Cu^{2+} specificity and quench the fluorescence of CDs. While adding L-cysteine in the solution of CDs-Cu^{2+}, Cu^{2+} could be released from the surface of the CDs, thereby recovering the fluorescence of CDs. With these chemical sensors, which successfully detected Cu^{2+} and L-cysteine, two substances, the detection limit was 2.3×10^{-8} mol/L and 3.4×10^{-10} mol/L, respectively (Figure 9). Du et al. [62] take the same way, take I replacing the Hg^{2+} bound with CDs, successfully detected the iodide in aqueous solution.

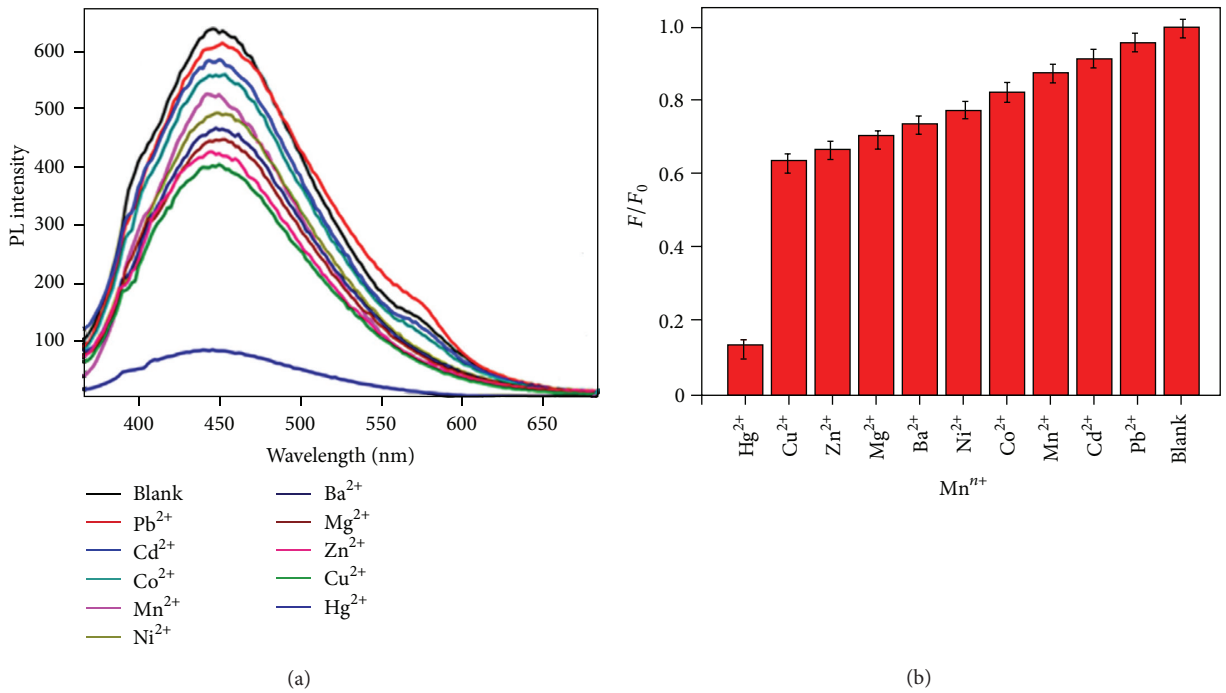


FIGURE 7: (a, b) PL spectra and the different PL intensity ratio (F/F_0) of the FCDs solution with various metal ions (at the same metal ions concentration of 1 mM).

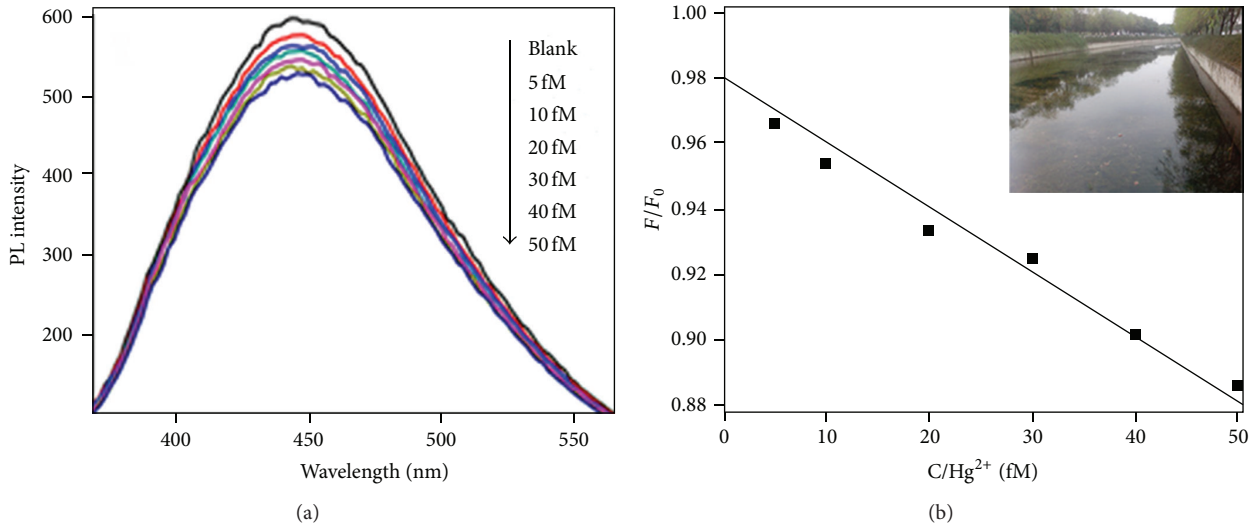


FIGURE 8: (a, b) PL spectra and the different PL intensity ratio (F/F_0) of the FCDs with various Hg^{2+} ions concentrations in the range of 0–50 fM in river water (reproduced with permission from [53]).

4.4. Biosensor. In 2011, researchers first achieved the detection of DNA; Bai and other studies [63] have found that methylene blue can effectively quench the fluorescence of CDs; then they joined ct-DNA in solution; the fluorescence of the solution was found to be restored. Based on this phenomenon, a new fluorescent sensor for DNA detection was designed; the detection limit was 1.0×10^{-6} mol/L with the linear ranging from 3.0×10^{-6} mol/L to 8.0×10^{-5} mol/L.

Xu et al. [64] described aptamer-functionalized CDs as a sensor for protein detection. Since the thrombin has two different combine sites, the presence of thrombin could induce the CDs and aptamer to form a sandwich structure (Figure 10). The sensor shows high specificity and sensitivity towards thrombin. The detection limit of this sensor reaches 1 nmol, which is improved compared with the other reported fluorescence-based thrombin detection assays.

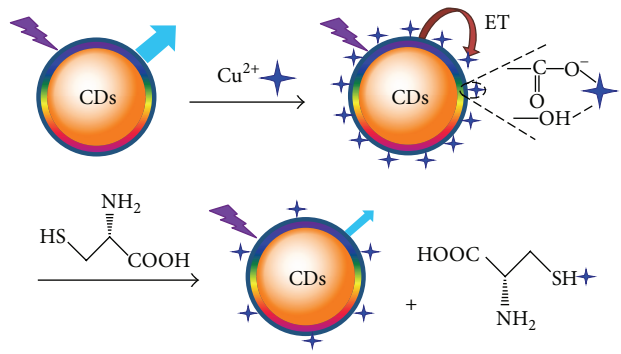


Figure 9: Carbon dots detection mechanism Cu^{2+} and cysteine (reproduced with permission from [42]).

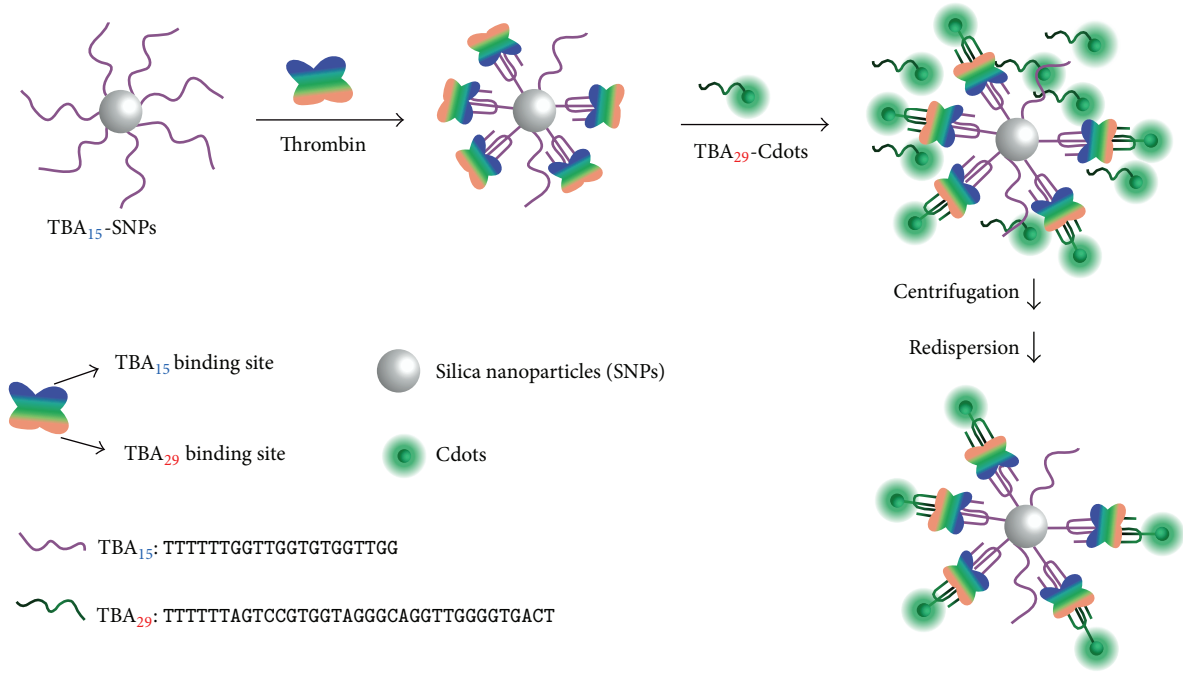


Figure 10: Schematic illustration of the sandwich-based thrombin detection principle using the carbon dots (reproduced with permission from [64]).

4.5. Bioimaging. We have already learned that the fluorescent CDs possess great advantages comparing with the traditional semiconductor quantum dots, including their outstanding optical properties and stable chemical properties; moreover, CDs are environmentally friendly and low toxicity nanomaterials. These characteristics make it possible that CDs replace semiconductor quantum dots in biological imaging [65].

Sun's team is the first research group that applied fluorescent CDs in bioimaging. They cultured MCF-7 cells vaccination in medium containing CDs for 2 h; fluorescent microscope was used to observe the fluorescence of cells; it was found that the fluorescence area is mainly concentrating in the cell membrane and cytoplasm [9]. Then Wang et al. [66] used vitamin B as precursor synthesized low toxicity and good biocompatibility fluorescent CDs via hydrothermal method and successfully applied it in U87 cell imaging. The U87 cells were seeded in the medium containing CDs for cultured 2 h; with a focus fluorescence microscope, it was found that only cell membrane and cytoplasm emit bright fluorescence, while the nucleus has not been invaded by CDs [61].

Zhang et al. [67] used lactose as a carbon source and 3-hydroxymethyl amino methane as carbon surface passivation agent to get high light, low toxicity fluorescent CDs via hydrothermal method. The study shows that the fluorescent intensity of the fluorescent carbon dots in the environment is not affected by the change of fluorescence intensity and the fluorescence intensity is still not affected by the salt solution and these CDs were successfully applied in HeLa cell imaging (Figure 11).

Yang et al. [24] take the purified CDs injected into female DBA/1 mice body by three ways of subcutaneous injection, intradermal injection, and intravenous injection and get successful in vivo imaging under light irradiation of 470 nm

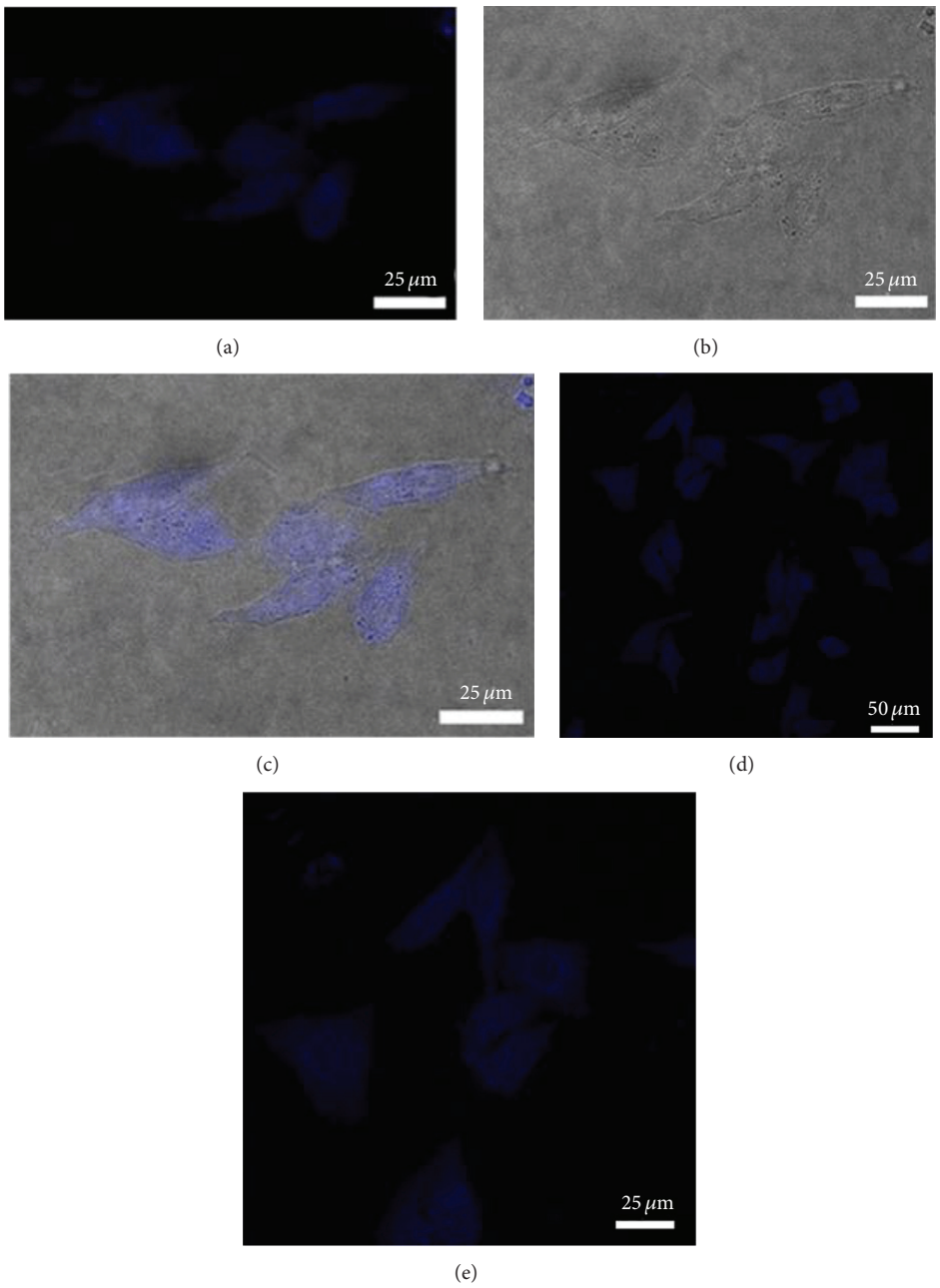


Figure 11: (a, d, e) Confocal fluorescence image (λ_{ex}: 405 nm); (b) bright-field microphotograph of HeLa cells incubated with 200 μgmL^{-1} of CDs for 4 h and (c) overlay image of (a) and (b) (reproduced with permission from [67]).

and 545 nm. They found that CDs subcutaneously injected into the mice of the forelimb would migrate along the forearm to the axillary lymph nodes, while CDs of intravenous injection in the systemic circulation concentrated at the bladder area. They also found that the urine can be detected with fluorescence after 3 h by injection. 4 h later, the fluorescent CDs can exist mainly at the kidney of mice and slightly at liver through dissection. They speculated that polyethylene glycol could reduce the effective surface of CDs on the affinity to protein and makes CDs more difficult in uptake by the liver comparing with the previous nanoparticles and nanotubes.

Goh et al. [68] take advantage of the properties that CDs can combine with hyaluronic acid (HA) homologues and applied the composite of hyaluronic acid homologues and CDs (HA-CDs) successfully to hyaluronic acid imaging in vitro. They injected HA-CDs into mice through subcutaneous injection and observed the fluorescence on the mouse skin, validating the feasibility of HA-CDs imaging in vivo. Subsequently, they injected HA-CDs by means of intravenous injection manner into mice; after 4 h they get the distribution of HA in the liver, kidney, and spleen of the mice through the fluorescence microscope (Figure 12).

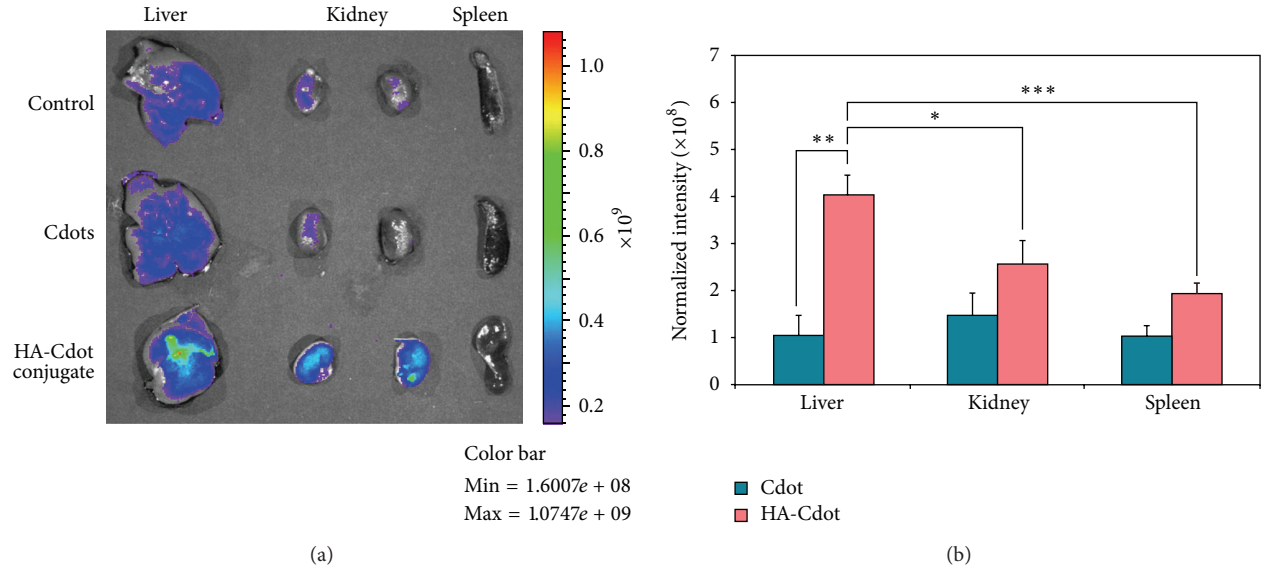


FIGURE 12: (a) Fluorescence image of dissected livers, kidney, and spleens 4 h after tail-vein injection of Cdots or HA-Cdots conjugates. (b) Quantitative fluorescence analysis of Cdots and HA-Cdots conjugated in the dissected organs ($^{*}P < 0.05$, $^{**}P < 0.005$, and $^{***}P < 0.001$) (reproduced with permission from [68]).

4.6. Drug Delivery. Traditional drug carrier does not have the observability and traceability; thus the researches that applied fluorescent nanomaterial to the drug carrier are expected to solve these problems. Due to its low toxicity, excellent biocompatibility, and modifiable surface function groups, CDs have become a hot spot of drug delivery research.

Lai et al. [69] employed glycerol as the carbon source and prepared CDs by pyrolysis. After that, they modified the CDs via PEG and controlled the particle size through mesoporous nanoparticles to obtain uniform and excellent optical properties of CDs (CDs @ mSiO2-PEG). The CDs @ mSiO2-PEG can be used as an anticancer drug doxorubicin (DOX) carrier and the release rate of DOX was studied in HeLa cells. The results showed that CDs and DOX in the cytoplasm and nucleus emitted blue fluorescence and red fluorescence, respectively. According to the proportions of the two fluorescent colors, this method can achieve a pharmaceutical carrier and observability traceability by in situ monitoring of DOX in cells release rate.

Zheng et al. [70] combined amino groups on CDs surface with oxaliplatin through the chemical coupling reaction, with the two substances incorporating as one. The modified CDs can enter into the interior of cancer cells via endocytosis. Due to the rapid changes in the internal environment of the cancer cells, the drug can be released from the surface of the CDs. The results showed that by monitoring CDs fluorescence signal in cancer cells they can fully understand the distribution of oxaliplatin in cancer cases, which will provide great help for doctors to grasp the exact time and dose drug injection.

5. Summary

As a new category of nanomaterials, fluorescent nanomaterials have outstanding optical properties, good biocompatibility, and surface functional division of regulatory and other characteristics; thus they have been studied extensively in photocatalysis, biochemical analysis, bioimaging, drug delivery, and other areas and show great potential and are promising in these fields. However, as a budding member of the family of carbon nanomaterials, the application ranges of fluorescent CDs should still be further improved and make sufficient use of surface rich functional groups on CDs, broadening their composite structural applications in various fields. Although fluorescence CDs realized the great-leap-forward from in vitro imaging to in vivo imaging, the emission fluorescence of most of CDs is distributed in ultraviolet region or short wavelength visible region, which limits the optical imaging in life body for deep tissue. In addition, almost all of life organisms will produce autofluorescence under short wavelength UV and visible light radiation, which often interfere seriously with the visual effects. Therefore, the development of fluorescent CDs in near-infrared region is urgently needed in the future. Moreover, the current researches on in vivo imaging merely stay in the experimental stage for small animals; further progress for the live animal imaging needs to be promoted. The optimization of preparation process of fluorescent CDs and the development of green, convenient, and low-cost methods for preparing CDs with fine physical, optical properties both can be addressed further.

In a word, CDs are novel fluorescent nanomaterials with outstanding fluorescence properties. They have numerous

excellent applications in a variety of fields involving chemical and biological sensing, biological imaging, drug delivery, and photocatalysis, which are greatly promising for the future development.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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