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Review

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The production and properties of carbon dots

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ABSTRACT

Carbon Dots (CDs) are a new kind of fluorescent nanomaterials developing fast in recent years. There are many articles on preparing CDs by different methods. However, summarizing and comparing these different synthesis routes, further more studying on the reason why their applications are limited in vitro was seldom reported. Herein, the property, synthesis, modification and application of CDs are comprehensively reviewed. This review focuses on CDs' unique properties such as low toxicity, stable fluorescence intensity and comparing the existing synthesis methods including the top-down and the bottom-up, the applications in bioimaging and analysis are also stated.

KEYWORDS

Carbon dots;
Synthesis routes;
Properties;
Applications.

INTRODUCTION

Quantum dots (QDs) are composed of atoms from groups II–VI (such as CdTe, ZnS), III–V (such as GaAs, InP) or VI- VI(such as PbS, PbSe) elements which have attracted great attention owing to their mature synthesis routes and the strong, stable, narrow band luminescence[1]. However, the potential toxicity and relative large size of QDs may limit their applications. CDs have a lot of unique optical properties and exhibit advantages over QDs such as low toxicity and good biocompatibility, which make them potential in the fields of bioimaging, analysis, etc.

CDs are a new type of fluorescent nanoparticles, they possess small dimension[2-4], stable fluorescent performance[5], tunable excitation and emission spectrum[6], low toxicity, eco-friendly characteristics[7,8]. They have great superiority to take place of the toxic semiconductor QDs[9] or other carbon nanomaterials including fullerene[10-12], carbon nanotubes[13] and carbon nanofibers[14,15] to be applied in a broad range of fields. CDs have the potential in bioimaging, medicine and analysis fields, they might be applied in biosensing and biochemical analysis[16] as well. However, researches on CDs are still in the initial stage: synthesis routes remained inadequate; the fluorescence quantum yield had yet to be improved; the application was limited in bioimaging and quantitative analysis. Therefore high quantum yield sythesis routes are in urgent need to expand the applications of CDs.

Here we review the properties of these carbon nanoparticles; the synthesis including the top-down and bottom-up methods and the modifications involving three different aspects to increase the fluorescence quantum yield, the comparisons among them are also elaborated.

Review

PROPERTIES OF CDS

Water-soluble and functionalized property

The surface of CDs was usually modified with a lot of carboxyl and hydroxyl groups due to the special preparation process which made them water-soluble[5,17] and functionalized easily by different organic molecules and polymers, etc. The functionalized groups on the surface expanded the applications and improved the fluorescence intensity[6,18]. Zhou's[5] group prepared water-soluble CDs by watermelon peels. The XPS (X-ray Photoelectron Spectroscopy) and FTIR (Fourier Transform Infrared spectroscopy) spectrums were shown in Figure 1. The XPS spectrum showed the two main peaks of carbon atom: 284.5 eV (C-C, sp^3) and 287.8 eV (C = O, sp^2), indicating the exist of hydrophilic groups on surface of CDs. In the FTIR spectrum, 1580 and 1633 cm^{-1} peaks were belonged to the C = O stretching vibration absorption, while 3413 cm^{-1} peak was attributed to OH^- stretching vibration absorption, all those peaks demonstrated the presence of carboxyl and hydroxyl groups on the surface of CDs.

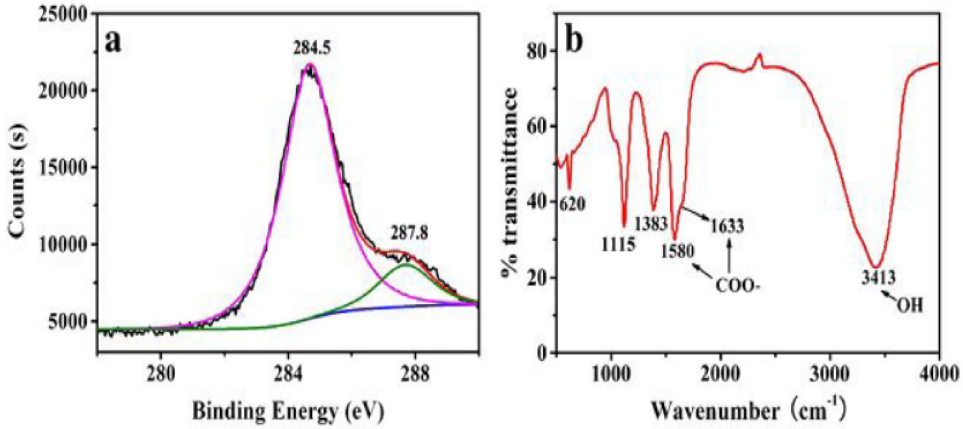

Figure 1 : (a) The XPS (C-C, sp^3: 284.5 eV; C = O, sp^2: 287.8 eV) and (b) FTIR (C = O: 1580 and 1633 cm^{-1}; OH^-: 3413 cm^{-1}; b) spectrum of CDs

Small molecular weight and particle size

Comparing with the traditional organic fluorescent dyes, the particle sizes of CDs are large[19-22], but they were samller than semiconductor QDs. Figure 2 is the HRTEM (High Resolution Transmission Electron Microscopy) image of CDs. The molecular weight of them ranged from thousand to tens of thousands[23-25]. The relative small particle size of these nanomaterials make them easy to enter into cells through endocytosis, this property makes the appplication in cell marking and biological imaging possible.

Stable fluorescence intensity

After a long period irradiating of exciting light, the fluorescence intensity of conventional organic fluorescent dyes would decay rapidly, which may limit their application in biology labeling. However, CDs can overcome these shortcomings due to their stable luminescence intensity at a large pH range (pH 2.0~11.0) and a high salinity concentration (0.02mol/L,NaCl)[5]. Mao et al[26] showed the fluorescence of CDs produced by industrial lampblack and passivated with PEG1500N were stable in water solution for more than half a year. The laser scanning confocal microscope experiment[27] also indicated that the fluorescence of CDs was constant after hours of excited light irradiating.

Wide and continuous excitation spectrum

Generally, the organic fluorescent dyes had a narrow excitation spectrum and different dyes were excited by different excitation wavelength. The obtained fluorescence peaks were broad, asymmetric and overlapped, which could not be analyzed simultaneously. However the excitation spectra of CDs was wide and continuous, which ranged from the ultraviolet spectrum to the visible spectrum and the emission spectra was narrow, symmetrical and lightly overlapped[27,28]. Therefore the single fluorescence excitation can lead to wide band emission spectra. That is to say, when they are excited by a kind of short wavelength light, CDs can emit different wavelengths fluorescence light, which makes the simultaneous analysis possible.

Photoluminescence property

Photoluminescence means the emission wavelength and intensity depend on the wavelength and intensity of exciting lights. Liu et al[6] synthetized CD-PEI (polyethylenimine) by microwave asssisting method, the fluorescence microscopy images at different exciting wavelengths are as follows (Figure 3a). Blue, green, red fluorescence were shown from left to right; Changing exciting wavelength (from 340 to 500nm), the peak positions of emission spectrum were also changed, and the range of modulation was quite wide from visible region to the near infrared region (Figure 3b) while the organic fluorescent dyes could not be excited in the near infrared region. Photoluminescence of CDs was an absolute advantage in cell labeling because CDs can emit different fluorescent colors by changing exciting wavelenghth and that is convenient for observation and recognition.

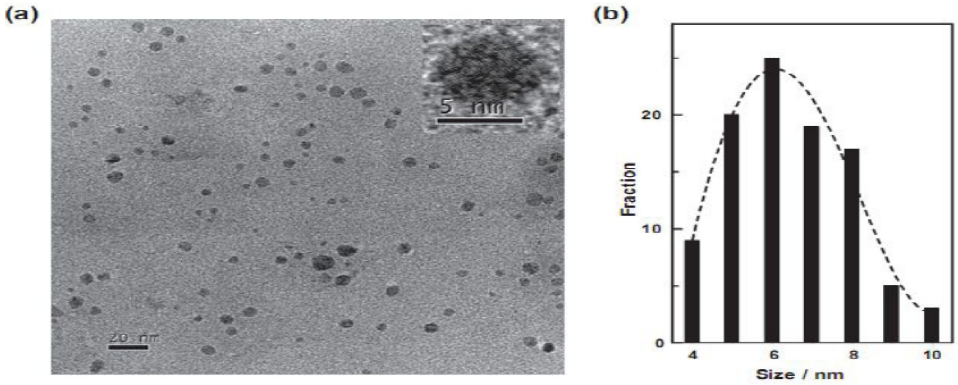

Figure 2 : HRTEM (a) and particle size distributions (b) of CDs

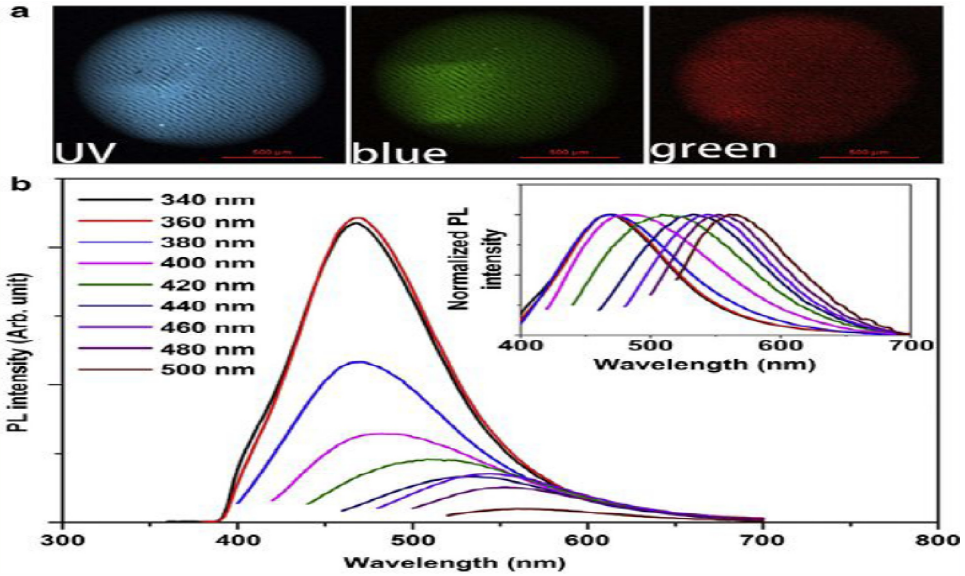

Figure 3 : (a) CD-PEI aqueous solution at different emission lights (from left to right is violet, blue and green) (b) photoluminescence spectrum and luminous intensity spectrum of CD-PEI

Photoinduced electron transfer property

CDs are good electron donors and recipients due to their electron withdrawing and donating groups on their surface, which will lead to electron transfer and quenching in polar solvent when combining with other electron donors or recipients.

As literature[29] stated, the fluorescence of CDs obtained from laser ablation method was quenched at 425nm in methylbenzene solvent while adding electron recipient 4-nitrotoluene and 2,4-dinitrotoluene; meanwhile, the fluorescence of electron donor N,N-dieththyaniline could be quenched by this kind of CDs.

The electrochemical luminescence property

Semiconductor QDs exhibit ECL (exciting electro-

chemical luminescence) property and are widely used in optoelectronic device and biological marking. CDs showed excellent electroluminescent property similar to the semiconductor ones while they are nontoxic. The ECL of CDs produced from the electrochemical oxidation of graphite was observed obviously on the graphite electrode. The ECL intensity was higher than the reference substance without CDs[30].

Low toxicity and good biocompatibility

Semiconductor QDs have already been used in cell and vivo imaging, but even low concentration of them may cause the cells to die due to the toxic metals such as Cd, Dy[31,32]. There were still a lot of cells dying although researchers tried to reduce their toxicity by modifying organic polymer on the semiconductor QDs. CDs are expected to be an ideal material for biological fluorescent labeling with the properties of perfect optics, small particle diameters, nontoxicity, good biocompatibility and little damage to cells, etc[7,8].

SYNTHESIS AND MODIFICATION OF CDS

CDs are a kind of spherical nanoparticles with diameters lower than 10nm. They could not be applied in fluorescence labeling and bioimaging without modification due to the weak fluorescence. The synthesis of CDs are usually classified into two parts: the top-down and bottom-up methods. The top-down method means CDs are generally formed through post-treating the carbon particles broken from a large carbon structure, consisting of arc discharge, laser ablation, electrochemical oxidation; The bottom-up approach comprises combustion, thermal carbonization, acid dehydration and ultrasonic treatment by which CDs are transformed from suitable molecular precursors, and then purifying them by centrifugation, dialysis, electrophoresis or other seperation methods.

Top-down synthesis method

Extrating from Arc-discharged soot

Xu et al[23] found the fluorescent nanoparticles (CDs) by extracting the single-walled carbon nanotubes (SWCNTs) from arc-discharge soot with preparative electrophoresis in agarose gel and glass bead matrixes and oxidizing them with HNO_3 to ensure the carboxylate group modifying on the surface of CDs. Then separating the SWCNTs and the short tubularmaterial (CDs) by preparative electrophoretic method from the obtained suspension, three kinds of CDs with different sizes and luminescent properties would be separated during further treatment.

Laser ablation method

Sun et al[33] got many nonluminous CDs with different sizes by laser ablation of a carbon target in the presence of water vapor with argon as carrier gas, then refluxed them with nitric acid aqueous solution and reacted with surface passivation to get strong fluorescence. Controlling the reaction condition rigidly CDs with diameters of 4~5nm could be obtained.

Hu et al[34] irradiated the suspension liquid of carbon powders in organic solvent by laser. The surface modification was finished simultaneously with the formation of CDs and tunable emission light could be generated in the appropriate solvents. CDs with about 3nm diameter were obtained after irradiating by Nd:YAG pulse laser and centrifugation, researchers also got similar sizes of CDs by laser irradiation, oxidization, passivation in one stage. The origin of the luminescence was attributed to carboxylate ligands on the surface of CDs.

Electrochemical oxidation method

CDs were performed by Zhou et al[35] in a degassed acetonitrile solution with 0.1M TBAP (tetrabutylammonium perchlorate) as the supporting electrolyte, MWCNTs as working electrode, an Ag/$AgClO_4$ as reference electrode and a Pt wire as counter electrode (Figure 4). The obtained CDs have uniform spherical shapes and narrow size distributions with diameter of 2.8 ± 0.5nm. These CDs possess relative high efficient luminescence, but the complex synthesis routes and the heavy metal in the electrolyte limit their mass preparation and makes the further application in biology difficult. Chi et al[30] used the similar route preparing CDs with diameters of 2 and 20nm by electrochemical oxidating the graphite rod.

Two types of fluorescent CDs were obtained through similar electrochemical oxidation methods by Zhao et al[27]. They were blue fluorescent dots with molecular weight <5KDa and yellow ones with 5~10KDa. The advantage of this method was that the reaction took place in water solution and it was easier

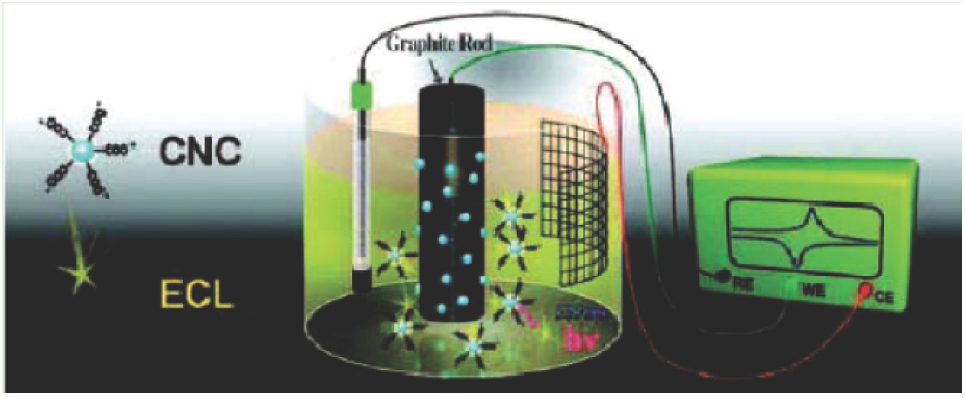

Figure 4 : CDs prepared by electrochemical way from a graphite rod

than the former one.

Lu et al[36] found a facile way to generate fluorescent nanoparticles by ionic liquid-assisted electrochemical exfoliation. This approach generated the exfoliated graphene sheets directly from graphite and ILs have been proposed as "green" alternatives to conventional solvents. Strategies were developed to control the distribution of the exfoliated products and the fluorescence of these carbon nanomaterials could be tuned from the visible to ultraviolet region by controlling the water content in the ionic liquid electrolyte.

Bottom-up syntehsis method

Chemical oxidation method

Mao et al[26] collected the candle soot by putting a glass plate on top of the smoldering candles and refluxing the candle soot with HNO_3, then purifying them through centrifugation, dialysis and ultra filter to obtain small (<2nm) and water soluble CDs.

The same carbon source-carbon soot was used to prepare CDs by Ray et al[10], but the purification method was improved by centrifuging them to get rid of unreacted carbon soot and mixing with acetone (water/acetone volume ratio was 1:3), then centrifuging again to collect the black precipitate. Finally CDs with diameters of 2~6 nm were obtained. This method simplified the purified stages and reduced the reaction time simultaneously.

Tian et al[37] used natural gas soot as starting material, then refluxed them with HNO_3 for 12h and dialyzed by nanopure water to get the purified carbon nanoparticles. The average diameter of the carbon nanoparticles was found to be 4.8 ±0.6 nm.

CDs with diameter of 2.0 ± 0.5 nm have been synthesized by Zhou et al[6] through low-temperature carbonization, then treating them with simple filtration (0.2μm millipore filter), centrifugation (18000 r/min020 min) and dialysis (48h) using watermelon peels which were waste, reproducible and novel carbon resource (Figure 5). This easy approach allowed large-scale production of CDs aqueous.

Figure 5 : The synthesis of water-soluble fluorescent CDs from watermelon peel

Carrier method

Liu et al[38] report a novel and straightforward route to prepare CDs (1.5~2nm) with amorphous structure through employing surfactant-modified silica spheres as carriers. Firstly, satellite-like polymer/F127/silica composites were prepared by an aqueous method using resols (phenol/formaldehyde resins, Mw<500) as carbon precursors and silica colloid spheres with

functionalized amphiphilic copolymer F127 as carriers. F127 played an important role in the preparation process of hydrogen bonding with resols. Then CDs/silica composites were obtained by heating treatment under N_2, furthermore removing the silica template to get the released CDs.

Bourlinos et al[2] prepared CDs using NaY zeolite as the carrier. First exchanging NaY zeolite with 2,4-diaminophenol dihydrochloride followed by thermal oxidation in the air, the exchange took place mostly near the external surface of the zeolitic crystallites and proceeded little within the host structure. Oxidation would make nanoparticles residing mostly on the surface of the zeolite matrix. Carbon nanoparticles with sizes of 4~6nm would be obtained by etching C-ZEO (carbon zeolite matrix) with hydrofluoric acid and the surface-treated C-ZEO exhibited similar luminescent behavior to the dispersed nanoparticles.

Carbohydrate carbonization method

Peng and Travas[4] used carbohydrates as starting materials and dehydrated them by concentrated sulfuric acid to produce carbonaceous materials. The obtained carbonaceous materials were then broken down into individual carbogenic nanoparticles by treating them with nitric acid. Finally, the carbogenic nanoparticles were passivated by amine-terminated compounds, then yielding luminescent carbogenic dots were received.

Zhu et al[39] reported microwave assistant method by dissolving PEG200 and carbohydrates in water solution, then microwave-heating them. In this method synthesis and passivation were finished in one stage.

In the experiment of Bourlinos et al[3], the citrate served as the carbon source and the organic ammoniumion as the surface modifier. The solubility of CDs changed with the surface modification group. The fluorescence emission peak of hydrophilic CDs was not affected by the excitation wavelength in the range of 400~500nm. The different synthesis methods above were summarized here. (TABLE 1)

Modifications of CDs

The performance of CDs is superior to many semiconductor QDs, but the lower quantum yield restricts their applications. CDs modification means mixing CDs with modifier and integrating the modifier to the surface of them. The optic property and the fluorescence quantum yield of CDs will increase after surface modification. Generally, the modification methods include passivation, doping and clad metal.

Surface passivation method

In the laser ablation method, the fluorescence quantum yield was lower when using PPEI-EI (propionylethylene- imine-co-ethyleneimine) as a passivator compared with PEG1500[33].

Dong et al[18] synthesized CDs by carbonizing citric acid with BPEI (branched polyethylenimine) at the low temperature (<200 °C) in one simple step. It was the first report that CDs were both amino-functionalized and highly fluorescent, which suggested their promising application in chemical sensing field. (Figure 6)

Mechanistically, the passivator may minimize the impact of surface-defect states; Another way of saying it was, the photoluminescence from CDs may attribute to the presence of surface energy traps after surface passivation. The common passivators include organic molecules with hydroxy, carboxyl or amidogen groups such as TTDDA, PEG1500, N-acetyl-L-cysteine and polyethylene glycol such as PEG6000PEG2000.

Doping method

One typical example of this passivating effect was proposed by Sun et al[40], the quantum yields of CDs would increase to 50%, 45% when doping with ZnO or ZnS. The dopant would provide secondary yet more effective surface passivation in combination with the organic passivation agents, ZnO-CDs and ZnS-CDs in aqueous solutions are competitive to the commercially available organic-based CdSe/ZnS QDs in luminescence brightness and they have been applied in optical imaging successfully.

Clad metal method

In the experiment of Tian et al[37], metal salts ($AgNO_3$, $Cu(NO_3)_2$, $PdCl_2$) were added into nanostructured materials, then adding ascorbic acid dropwise. The metal ions most likely bound to the peripheral carboxylic moieties by ion exchange or coordination reactions. Upon the addition of a reducing reagent, the metal ions were reduced to metal atoms, which served as the nucleation seeds for the growth of metal nanostructures. On the basis of these measurements, the CDs obtained above most probably

functionalized with carboxylic/carbonyl moieties on the particle surface. Interestingly, these nanoparticles exhibited unique photoluminescence properties. The problem with this approach was that the diameters of spherical metal were much larger than the normal ones and that was a barrier in bio-labeling and intravital imaging application.

The comparation of the three modification meth-

TABLE 1 : Comparison of different synthesis methods

Synthesis methods		Carbon sources	equipments	reaction condition	The quantum yields and particle sizes	references
Top-down	extrating from Arc-discharged soot	single-walled carbon nanotubes	preparative eletrophoresis	Agarose gel and glass bead matrixes	1.6% at 366nm excitation diameter:1nm	[23]
	Laser ablation method	carbon target	Laser	the presence of water vapor with argon as carrier gas	4～10% at 400nm excitation diameter: 4～5nm	[33,34]
	Electrochemical oxidation method	graphite	electrolytic cell	electrolyte electrodes	2.8-5.2 % diameter: 2～4nm	[27,30,35,36]
Bottm-up	Chemical oxidation method	candle soot, natural gas soot	reflux device	Heating, stirring	3% at 450nm excitation diameter: 2～6nm; the lifetime of passivated CDs is longer than the bare one	[6,10,26, 37]
	Carrier method	resols (phenol/formaldehyde resins, Mw<500)	silica colloid spheres with functionalized amphiphilic copolymer F127 as carriers	heating treatment under N_2	11～15 % at 458,488, 514nm excitation; dimeter: 1.5～2.5nm	[2, 38]
	Carbohydrate carbonization method	carbohydrates	Heating device	Heating	3.1-6.3% at 340nm excitation diameter: <10nm	[3,4,39]

Review

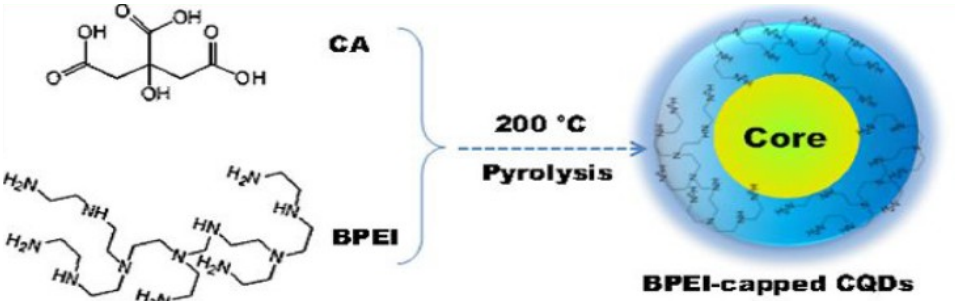

Figure 6 : The synthesis of BPEI-CDs

TABLE 2 : Comparison of different modification methods

Modification Methods	Surface passivation	Doping method	Clad metal method
Reaction	The passivators acted with the surface groups of CDs	CDs were doped with ZnO or ZnS	Metal salts and ascorbic acid were added into CDs
The quantum yields	42%	45～50%	33～60%

ods were summarized as below (TABLE 2).

General review

So far, the synthesis methods of CDs varied with both advantages and disadvantages. Special devices and instruments were needed in electrochemistry method which made the reaction complex and made synthesis in large scale difficult, therefore the synthesis routes have transfered to the easy chemical oxidation method, but the low fluorescence quantum yields limited their application in many fields. Improving the synthesis methods to make a easy, effective, high fluorescence quantum yield way will be vital meaningful in the future.

The groups on the surface of the synthesis naked CDs made it easy to combine with some modifiers. If the combination between them was stable, the fluorescence quantum yield would be high after modification and the application would be expanded.

APPLICATIONS OF CDS

Semiconductor QDs have been applied in cell[41,42] and intravital imaging[43], but the existing of heavy metals such as Cd, Dy made it great toxic even at low concentration, it may cause the death of cells[31,32]. CDs could be used as a biomarker to detect in vivo for long time due to the long lifetime fluorescence and steady property after hours of high density exciting light; Furthermore, CDs with different sizes exhibited different colors and the range of excitation wavelength was wide which made it easy to detect samples simultaneously. Moreover, they owned better bio-safety and less interference to biomolecule compared with the existing fluorescent materials.

However the undeveloped synthesis routes led to the low fluorescence quantum yield and limited the applications of CDs. It could only be applied in bioimaging, quantitative analysis by now. However, it has huge potential in vivo biosensing and biochemical analysis.

Application in bioimaging

As a to-be contrast medium used in bioimaging, the cytotoxicity of CDs appear crucial. Ray et al[17] trypsinizing and resuspending HepG2 cells in culture medium. Different amount of CDs solutions were loaded to each well. After incubation for 24h, cell viability was calculated by assuming 100% viability in the control set without any CDs through MTT (methyl thiazolyl tetrazoliym assay) and Trypan blue assays. The cell survival rate in <0.5 mg/mL was between 90% and 100%, suggesting a minimum cell death. However, at higher concentration, some percentage of cell death is observed. Yang et al[8] studied the cytotoxicity of CDs in mice, achieving the similar result.

Flurescent CDs were synthesized by Huang et al[7] through a solvothermal method with glucose as the carbon source. They investigated the dependence of yeast's growth on the concentration of fluorescent CDs at various growth periods (adjustment, initial and middle loga-

rithmic phases) by using saccharomyce cerevisiae yeast as a modle organism. The result showed that there was no influence on yeast's growth curve even the concentration of fluorescent CDs as high as 27.75mmol·L^{-1}. They also compared the yeast cytotoxicity of fluorescent CDs with CdTe QDs under the same fluorescent intensity, indicating a much lower cytotoxicity fluorescent of CDs than that of CdTe QDs.

This result concludes that CDs can be used in high concentration for imaging or other biomedical applications.

Bioimaging in vitro

An exploratory experiment of Cao et al[44] demonstrated CDs could be imaged in both cell membrane and cytoplasm, but not cell nucleus. Fist, they passivated CDs with PPEI-EI and marked human breast cancer MCF-7 cells by them, then incubating them for 2h at 37°C.The figure below was obtained through the two-photon luminescence microscopy, they also found that CDs could be phagocytized only over 4°C, otherwise, they could not enter cells.

Ray et al[17] led a conventional bioimaging research to EACs (ehrlich ascites carcinoma cell) using CDs (2~6nm) prepared by carbon soot.

Liu et al[6] applied CDs (1.5~2nm) prepared by carrier method to bioimaging in E. coli (escherichia coli). Figure 8 shows confocal microscopy images of E.coli cells labeled with CDs after a co-incubation of 24h, where the E.coli cells appeared to be completely covered by CDs. The photoluminescence can be collected with a broad range of excitation wavelengths (e.g.458, 488, 514nm), CDs were also found to be easily internalized in murine P19 progenitor cells.

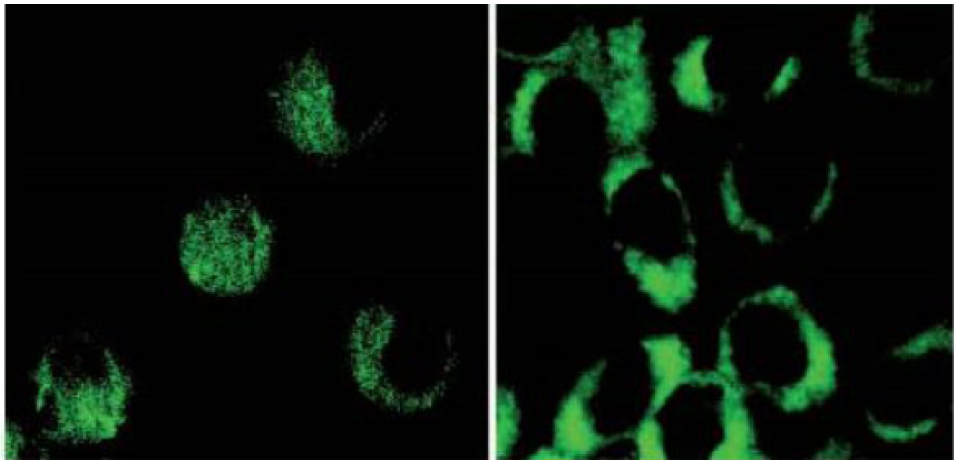

Figure 7 : Human breast cancer MCF-7 cells with internalized CDs

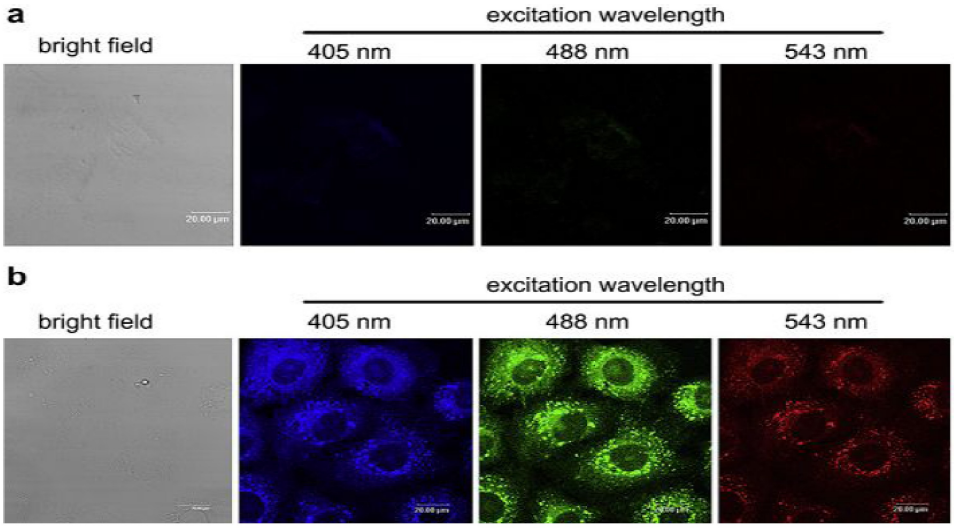

Figure 8 : Non-transfected cells as negative controls(a) and transfected cells(b).(The samples were observed under bright field, 405, 488 and 543 nm; All scale bars: 20μm)

Review

Bioimaging in vivo

The fluorescence medium in vivo should own the property of high fluorescent intensity and stability, nontoxicity, biocompatibility.

Yang et al[45] reported the first study of CDs for optical imaging in vivo: injecting PEGylated (polyethylene glycol) CDs and ZnS CDs in BA/1 mice by three different ways (subcutaneously injection, intravenously injection, intradermal injection), then they found the subcutaneously injected mice exhibited the brightest emissions from CDs and ZnS CDs, the relative strong fluorescence from the latter was consistent with the previously reported solution-phase results. CDs in mice diffused relatively slowly and the fluorescence was faded after 24h postinjection. Unlike semiconductor QDs such as CdSe/ZnS, which could migrate to axillary lymphnodes in minutes, the observed migration of the CDs was slower. This could be due to small sizes of CDs and/or the surface functionalization by PEGs, whose protein resistance characteristics might reduce the interactions of CDs with lymph cells. The result suggested that the intravenously injected CDs were primarily excreted through urine, an excretion pathway that had been widely reported in the literature for PEGylated nanoparticles[46]. There was no toxic reaction during the whole experiment,which indicated CDs were fine fluorescence labelling and imaging materials. (Figure 9)

Therefore CDs are good fluorescence labeling and imaging reagent which could be used in biomedicine and optical imaging.

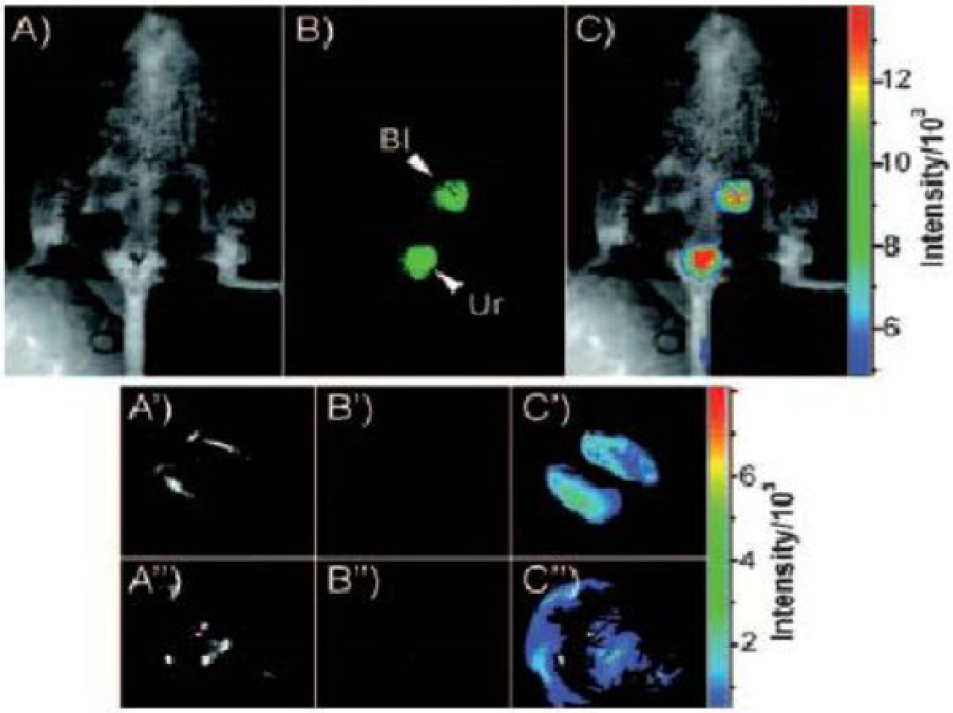

Figure 9 : Intravenous injection of CDs: bright field (A), as-detected flurescence (B1, bladder; Ur, urine) (B), color-coded images (C). The same order is used for the images of the dissected kidneys (A'-C') and liver (A"-C")

Application in analysis

Ions detection

Helena et al[47] prepared carbon nanoparticles functionalized with NH_2– PEG 200 (polyethylene-glycol) and NAC (N-acetyl-l-cysteine), they found the fluorescence intensity of the nanoparticles was quenched by the presence of Hg(II) and Cu(II) ions with a Stern–Volmer constant (pH = 6.8) of 1.3×10^5 and $5.6 \times 10^4 M^{-1}$, respectively. Therefore they referred functionalized CDs could be used as a novel biocompatible nanosensor for measuring Hg(II).

Wang et al[29] mentioned that photoluminescence from CDs was quenched efficiently by either electron acceptor (2-nitrotoluene and dinitrotoluene) or electron donor (diethylamine) molecules. That means photoexcited CDs are both excellent electron donors and acceptors, which predicts their application in light energy conversion.

CDs obtained by Jorge et al[48] in laser ablation

method were fluorescent with excitation and emission wavelengths at 340 and 450nm, respectively, and the fluorescence intensity was quenched by Hg(II) and Cu(II) ions. The metal ions and functional groups on the surface of CDs would comprise the complexes. CDs were immobilized in a thin (about 750nm), homogenous and smooth film (roughness of 2.7±0.7A). The nanosensor showed a fast (less than 10s), reversible and stable response. Also, the nanosensor allowed the detection of sub-μmol concentrations of Hg(II) in aqueous solution.

Organics detection

Wang et al[24] referred that the PEG1500N modified CDs obtained by laser ablation method could be quenched by 2-nitrotoluene, 2,4-dinitrotoluene, N,N-dieththyaniline and DEA (diethylamine). 2-nitrotoluene and 2,4-dinitrotoluene were electron recipients while N,N-dieththyaniline and DEA were electron donors. Stern–Volmer constant explaned the existence of dynamic quenching system.

DNA probe

A CD-based strategy for DNA sensing was proposed by Zhang et al[49]. CDs from candle soot were used as an immobilization support for a labeled single-stranded DNA (ssDNA) probe, resulting in quenching. Double-strande DNA (dsDNA) was formed through hybridization reacting with the target DNA, the probe fluorescence recoveried after desorption of CDs and this could be measured quantitatively. Here the CDs were used as quenchers of the luminescent DNA probe.

Zhao et al[50] mentioned that a fluorescent phosphate off-on probe was developed based on the europium-adjusted CDs which synthesized by condensation reaction between citric acid and 11-aminoundecanoic acid. The complexation of Eu(III) ions by the carboxylic groups provoked the quenching of CD fluorescence that quantitatively recovered when Eu(III) dissociated to the complex phosphate ions.

General review

The nontoxic property of CDs make them a good replacement of the toxic semiconductor QDs in many fields. No doubt that the application prospect is bright, but the immature synthesis routes and low fluorescence quantum yield limit their applications only in bioimaging and quantitative analysis. With the development of the synthesis and modification technics, the application of CDs will embrace broad prospects in the near future.

FUTURE PERSPECTIVES

The synthesis perspectives

The synthesis method of CDs tend to simple, convenient and high quantum yield. Wang et al[51] synthetized CDs by microwave method in 1min, they pyrolysed the anhydrous citric acid in AEAPMS (N-(β-aminoethyl)-γ-aminopropyl methyldimethoxy silane) at 240°C, 1 min and it was reported that the fluorescence quantum yield of the obtained CDs reached to 47%.

Until now, the bottleneck of synthesis is quantitative analysis of CDs, the concentration of CDs is difficult to determine through gravimetric methods due to the fact that the number of the surface groups is difficult to identify and may varied greatly under different reaction conditions. Yu et al[52] reported the absorption spectrum method to determine the concentrations of QDs (CdSe, CdTe, CdS). They may provide reference to CDs quantitative analysis.

The modification perspectives

The surface of synthesized naked CDs wre riched in carboxyl group, then modifiers with amidogen were added to increase the fluorescence quantum yield. However, this would reduce the stability of CDs, the unstable CDs could not be used in vivo. Therefore trying to find a stable modifying way is vital important in the future.

The application perspectives

Even though CDs are nontoxic, their application was limited in vitro for years. There may be two main reasons for that, on one hand people can not explain the photophysics of their fluorescence clearly till now, on the other hand carbon elements also exsit in our body, so when CDs enter into human body, it may not be recogonised.

CONCLUSION

In recent years, more and more people have paid

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close attention to the environment-friendly carbon materials. As a new member of carbon family, CDs are popular due to its low biotoxicity and stable optical property. The future research area of them lies at exploring an easy, effective and high fluorescence quantum yield synthesis and optimization method to make the application in vivo possible. we have great confidence and await that one day we will benefit from these nanomaterials.

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