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Carbon-dot-based solid-state luminescent materials: Synthesis and applications in white light emitting diodes and optical sensors

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Abstract: Carbon dots (CDs) have been regarded as a new star in the family of carbon nanomaterials, and have been widely studied since they were accidentally discovered in 2004. CD-based solid-state luminescent (CD-SSL) materials have the advantages of being environmentally friendly, non-toxic and low cost, which makes them ideal candidates to replace rare earth/semiconductor quantum dot-based luminescent materials. However, because of their quenching caused by aggregation, it is a great challenge to retain their luminescent properties when they are transferred from solution to the solid state. This review gives a brief introduction to the synthesis methods for CDs, followed by a detailed description of the most widely used strategies for the preparation of CD-SSL materials and their typical applications in white light-emitting diodes and optical sensors. Finally, the shortcomings of current research on CD-SSL materials are discussed, and their future in the above-mentioned as well as other fields is briefly considered. **Key words:** Carbon dot; Nanomaterial; Luminescent; White light emitting diode; Optical sensor

1 Introduction

Rare-earth-doped inorganic phosphors are the mainstream of traditional fluorescent/phosphor applications. Except for lanthanum and lutetium, all lanthanides have the characteristics of visible light emission after absorbing ultraviolet (UV) or near UV light^[1]. However, the supply of rare earth is not stable on the whole, and the extraction and processing of rare earth elements are easy to cause environmental hazards due to open-pit mining and radioactivity of rare earthbearing ores^[2]. With the development of inorganic semiconductors, luminescent materials based on semiconducting quantum dots (QDs) are considered as the promising materials to replace rare-earth-based counterparts^[3, 4]. These materials have great potential in optoelectronic applications owing to their unique physical properties such as high photoluminescent quantum yield (QY), adjustable emission wavelength and wide absorption band which originate from the size quantization effect. However, they often have cytotoxicity due to the presence of heavy metal ions (such as Cd²⁺)^[5]. In addition, they are normally produced by heat injection, which is difficult to be scaled up. In recent years, various organic or carbon materials have been used to develop solid-state luminescent (SSL) materials, including organic dyes^[6, 7] and conjugated polymers^[8]. However, the QY and stability of these materials are still insufficient. Therefore, it is of great significance to develop high-quality SSL materials with low cost, high efficiency, stability, and environmentally friendly.

Carbon dots (CDs) are spherical or quasi-spherical carbon nanoparticles whose sizes are typically below 10 nm. In some reports, they are also termed as carbon quantum dots (CQDs) or carbon nanodots (CNDs). As a new category of carbon-based photoluminescent nanomaterials, CDs have attracted increasing attentions. With excellent chemical stability^[9], photostability^[10], biocompatibility^[11] and low toxicity^[12, 13], they have been widely used in various fields including drug delivery, photoelectric devices and biological imaging^[14, 15]. With the development of the synthetic strategies, CDs with desired emission

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wavelengths and high OY can now be prepared. However, it is still a great challenge to prepare efficient SSL materials using CDs as fluorescent/phosphorescent components^[16]. In recent years, efforts have been made to overcome aggregation-caused quenching (ACQ) of CDs in the solid-state, which will contribute to the preparation and applications of CDs-based SSL (CDs-SSL) materials. In this review, the progress of the research on CDs-SSL materials is summarized. After a brief introduction of the synthetic methodologies of CDs, the preparation methods of CDs-SSL materials will be presented from two aspects, i.e., the selection of solid matrix and the postfunctionalization of CDs. Then, the applications of CDs-SSL materials in white light-emitting diodes (WLEDs) and optical sensors will be discussed. Finally, a brief outlook will be given for this interesting class of photoluminescent nanomaterials.

2 Synthesis

2.1 Synthesis of CDs

CDs were first separated from single-walled carbon nanotubes (SWCNTs) extracted from arc-discharge soot by Xu et al in 2004^[17]. Subsequently, Sun et al. performed laser etching on the carbon target prepared with graphite powder and cement, followed by surface passivation with diamine-terminated polyethylene glycol (PEG1500N) to realize the purposeful preparation of bright and luminous CDs in the laboratory for the first time^[18]. With the development of properties and applications of this new type of carbon nanomaterials, many different synthetic routes have been reported, which can be roughly divided into two catergories, i.e., "top-down" and "bottom-up" (Fig. 1). The "top-down" methods usually use arc-discharge, laser etching or electrochemical oxidation to cut carbon-rich bulk materials^[19]. Similar to the initially developed carbon nanotubes, the selected raw materials also include carbon soot^[20], carbon fibers^[21], coal^[22, 23], petroleum and asphalt residue^[24-26]. In order to achieve a high QY, the surface of CDs are generally required to be passivated by polymers. In addition, biomass materials can also be used to prepare CDs^[27], such as kitchen waste^[28–30], hair^[31, 32], plant branches and fruits^[33–35]. The "bottom-up" methods mainly focus on the use of atmospheric heating, hydrothermal, solvo-thermal, microwave-assisted and plasma treatment for high-temperature condensation and carbonization of small molecules or polymers containing organic functional groups, which has gradually become the dominant method for the preparation of CDs^[36].



Fig. 1 Two main methods for the synthesis of CDs. (a-c) Preparation of CDs from (a) petroleum coke^[25], (b)vcarbon fibers^[21] and (c) wastes^[30], (d-f) preparation of CDs from (d) citric acid and urea^[37], (e) guanidine carbonate (b)^[38] and (f) resorcinol^[39]. Reprinted with permission.

Owing to the variety of CDs and the complexity of their structures, there is still no unified theory to explain the photoluminescence of all CDs. At present, there are two widely accepted mechanisms. One is determined by the abundant functional groups on the surface of CDs, which is called surface state^[40]. The results show that different functional groups in the surface state of CDs lead to the competition between different emission centers and non-radiative traps, which endow the CDs with fluorescence characteristics^[41]. The unique emission flow pattern generated by the post modification process determines the fluorescence characteristics of CDs^[42]. The other is determined by the quantum confinement effect or the conjugated π domain of the carbonaceous core^[43]. According to the different preparation methods and raw materials, the core of CDs can be the stacked structure like graphite, or the disorderly structure which is close to amorphous carbon. Typically, graphene quantum dots (GQDs) with a single-layer graphene core can be obtained by the "top-down" method^[44]. However, in some literatures, CDs obtained by carbonization of small organic molecules are also called GQDs^[45]. In addition, the boundary between CDs and other similar nanostructures such as polymer dots (PDs) is also not very clear. In this review, we will mainly focus on the CDs with traditional definitions, with a few exceptions related to GQDs and PDs.

2.2 Synthesis of CDs-SSL materials

When CDs are concentrated in solutions or solidstate, it will lead to the reabsorption of photoluminescence or the non-radiation effect caused by energy transfer between adjacent CDs^[46]. Therefore, most CDs show the phenomenon of ACQ. In addition, the organic carbon nuclei in CDs are easily degraded by long-term exposure to air. These factors limit the photoelectric properties of most CDs in the solid-state. To solve the above-mentioned difficulties, two methods are frequently adopted. One is to use an appropriate solid matrix for effective dispersion of CDs. The other is to choose special raw materials to prepare CDs for post-modification through appropriate chemical reactions. In the case, the aggregation of the cores of CDs is prevented by the steric hindrance of modified groups on the surfaces of CDs. In the following, we will briefly summarize the progress in this field in recent years.

2.2.1 Coating CDs with polymer/crystal

The ideal solid matrix should not only effectively disperse CDs to prevent ACQ, but also necessary to act as a mechanical support and provide protection against environmental interference. By choosing materials that are flexible, easy to expand, environmentally friendly, stable and mechanically robust as solid matrixes^[47], a variety of CDs-SSL materials with excellent performance have been obtained.

2.2.1.1 Polymer coating

Many polymers are highly transparent in the UVvis range and possess high thermal stability, great processability and universal compatibility for encapsulation of guests. The polymer matrix can suppress ACQ of CDs by regulating their aggregation state, thus effectively improves the luminescence of the

polymer/CD composites^[48]. It is the most common and effective method to obtain CDs-SSL materials at the moment. Wu et al. developed a strategy for polymermediated GQD assembly and encapsulation by combining GODs with melamine-formaldehyde (MF) microspheres. The obtained GOD-MF microspheres possess even particle size, satisfactory stability and adjustable white light emission (Fig. 2a)^[49]. The MF microspheres prepared by heating the mixture of melamine and paraformaldehyde had a highly branched and crosslinked network inside, which enabled the stable encapsulation of GQDs. The emission spectrum of GQD-MF microspheres extended from the blue region to the whole visible light range, and the long-wavelength emission increased with increasing the doping concentration. In a subsequent study, Hu et al. also used a similar approach to assemble the tricolor QDs into a polysiloxane (Psi) matrix^[50]. Blue-emitting CDs synthesized from citric acid (CA) by hydrolysis and the metal QDs emitting green and red lights were assembled into the Psi in an solution 1-[3-(trimethoxysilyl) aqueous of propyl]urea, and the QDs@Psi microspheres was obtained by hydrolysis and polymerization. The resulting hybrid exhibited remarkable enhancement of the emission due to the well dispersion of the luminophors. It also had excellent optical stability, high thermal stability and good fluorescence recovery. Sun et al. synthesized CDs or PDs by a one-step hydrothermal method. The CDs or PDs were then mixed with polyvinylpyrrolidone (PVP) and engineered into finely dispersed CD/PVP or PD/PVP powder by drying and grinding, in which the optical properties of CDs and PDs were well retained^[51]. Luk et al. prepared GODs-polyaniline composite films by polymerization initiated by chemical oxidation^[52]. TEM images showed that the distribution of GQDs in the polyaniline matrix was almost uniform (Fig. 2b-c). On the surface of the composite films was located charge trapping sites induced by the functional groups, imparting them controllable optical and electrical properties. Similar to PVP^[51], polyvinyl alcohol (PVA) is also a popular matrix for the encapsulation of



Fig. 2 (a) Preparation of GQD-MF microspheres with white emissions of high-quality through polymer-mediated GQD aggregation and encapsulation^[49],
 (b, c) low magnification and high-resolution TEM images of the PANI-GQD composite^[52], (d) schematic illustration of the formation mechanism of starch/CD phosphors^[61] and (e) UV-Vis absorption spectra of pure starch, g-CDs in water, and starch/g-CD phosphors^[61]. Reprinted with permission.

CDs^[53–56]. Barun et al. dispersed nitrogen-doped CDs synthesized by the hydrothermal method of CA and ethylenediamine in the PVA matrix and prepared a transparent film with very high performance of UVblocking and blue-light emission^[47]. As the concentration of dispersed CDs in the matrix increased, the UV absorption of the film material also enhanced, but the QY decreased. Other polymers such as polymethyl methacrylate (PMMA)^[39,57], polyn-vinyl carbazole (PVK)^[58], polydimethylsiloxane (PDMS)^[59] and polyurethane (PU)^[60] have also been used as matrixes for the preparation of different SSL materials by binding with CDs.

To make the bond between CDs and the matrix stronger, one approach is to select a matrix that also has abundant polar organic functional groups on its surface. Qu et al. selected starch particles with rich hydroxyl functional groups on the surface as the matrix and prepared starch/CD phosphors by simply mixing them with CDs synthesized by the hydrothermal method from CA and urea (Fig. 2d)^[61]. The CDs and

the matrix of starch could be effectively united by hydrogen bonds, and the CDs adsorbed on a single starch particle were in a well-dispersed state. Meanwhile, the starch matrix did not compete to absorb the excitation light of CDs nor its emission (Fig. 2e), thus producing efficient emission. You et al. used carboxymethyl cellulose (CMC), a hydrophilic polymer that also contains a large number of hydroxyl groups, as the matrix to combine with CDs to prepare a composite film with a uniform structure, excellent optical properties and high tensile strength^[62]. The property that the CMC matrix also did not compete to absorb the excitation light of the CDs nor its emission light preserved the intrinsic optical properties of individual CDs. Li et al. directly mixed and stirred the CDs prepared from phenylenediamine with cellulose in deionized water to prepare a new kind of CDs-grafted cellulose as hybrid materials^[63]. In this case, CDs could interact with cellulose and form hydrogen binds, so that the cellulose could lock the emission fluorophore effectively and inhibited their intramolecular motion to

avoid aggregation. Compared with the CDs in an aqueous solution, the QY obtained from the hybrid phosphor was improved from 8% up to 44%.

In some cases, polymers also exhibit weak photoluminescence. Fortunately, their photoluminescent properties usually do not conflict with the absorption and emission of CDs. Thus, they only exist as dispersive matrix in the composites. Cross-binding with optical materials can also promote the development of bioenergy.

2.2.1.2 Crystal coating

Crystal has the characteristics of a compact structure, high optical transparency and great stability. The crystal formed by inorganic salts is extensively used in the preparation of semiconductor QDs-based solid phosphors. For example, Otto et al. combined CdS QDs with various crystals of inorganic salts to form mixed crystals that maintained the strong luminescence of QDs^[64]. They proposed that in the formation of mixed crystals, inorganic salts first formed microcrystals with QDs as crystal nuclei, which isolated individual QDs to prevent aggregation. Subsequently, the microcrystals grew into larger crystals.

The lattice structure, crystal quality and structural compatibility with CDs are dependent on the types of crystals of inorganic salts. Thus it can be expected that when they are used as a protective framework of CDs, different properties of the target composites might be induced. In recent years, much progress has been made in this direction. For example, Kim et al. prepared fluorescent materials which were stable under UV irradiation and thermal treatment by embedding organosiloxane-functionalized CDs into crystals formed by NaCl, KCl and KBr^[65]. It was found that the CDs combined with the NaCl crystal had the best stability and showed the mildest decay rate. Inspired by the study on the biomimetic synthesis of calcium carbonate (CaCO₃), Guo et al. reported a method of synthesizing fluorescent CaCO₃/CD composites by simply adding aqueous solutions of CaCl₂ and Na₂CO₃ to an aqueous suspension of CDs followed by mechanically stirring and vacuum drying (Fig. 3a)^[66]. As a template, CDs guide the formation and assembly of

CaCO₂ nanocrystals, and the crystal phase was mainly calcite with the best thermal stability. The interaction between the calcium ions and the oxygen-containing groups on the surfaces of the CDs could connect adjacent CDs and avoided ACO. In a recent study, Liang et al. used a facile and rapid method to prepare a CDs@BaCl₂ composite during the recrystallization process of BaCl₂ induced by anti-solvent, where CDs were introduced into the crystals in situ as the seeds in heterogeneous nucleation^[67]. In the hybrid materials, the CDs retained their characteristic surface states, and the non-radiative electron-electron energy interactions occurred between the aggregated CDs were inhibited by the spatial confinement effect of BaCl₂. which impacted the hybrid materials favorable luminescent properties. Green et al. combined CDs with crystals formed by alkaline earth carbonate, sulfate and oxalate to synthesize room-temperature phosphorescent composites that exhibited strong photoluminescent properties and bright afterglow with sub-second lifetime (Fig. 3b)^[68]. The excitation lifetime, steady state and afterglow color of the composites could be controlled systematically by changing the cation and anion in the matrix due to the influence of the properties of the matrix on the transition of emitted and nonemitted electrons. Some other inorganic crystalline materials such as zeolite (aluminum potassium silicate)^[69] and alum (aluminum potassium sulfate)^[70] have also been used as dispersion substrates for CDs.

Protein crystals usually have highly porous structures (porosity between 25 vol% and 60 vol%, pore size between 0.5 and 10 nm, pore volume 0.9– $3.6 \text{ mL} \cdot \text{g}^{-1}$ and total surface area between 800 and $3 000 \text{ m}^2 \cdot \text{g}^{-1}$)^[71] and can accumulate functional molecules from solutions^[72]. They can also be used as three-dimensional (3D), ordered substrates for the preparation of host-guest solid materials^[73–75]. However, unlike inorganic crystals, protein crystals such as those from lysozymes are heat sensitive and prone to denaturation under adverse conditions. In addition, they have high solubility and high permeability to gaseous molecules, which makes it difficult for them to meet the standard of being matrices for dispersion



Fig. 3 (a) Schematic illustration of bioinspired synthesis of fluorescent CaCO₃/CD hybrid composites^[66], (b) visualization of the integrating folic acid-derived carbon nanodots (F-CNDs) in inorganic single crystals. Optical microscopy images (b₁-b₅) and confocal fluorescence microscopy (CFM)

images (b_6-b_{10}) of CaCO₃ (b_1, b_6) , CaSO₄·2H₂O (b_2, b_7) , SrSO₄ (b_3, b_8) , CaC₂O₄·H₂O (b_4, b_9) , and SrC₂O₄·H₂O $(b_5, b_{10})^{683}$, (c) illustration of the preparation of the metal-free phosphor, (d) a typical optical image of the crystals. (e) and (f) SEM images of the crystals^[79]. Reprinted with permission.

of CDs in both liquid and gas phases^[76]. In this connection, England et al. used pentanediol to stabilize tetragonal lysozyme crystals in advance and directly synthesized CDs by further microwave heating and sodium borohydride reduction in a mixed solution of CA and ethylenediamine within the nanoscale channels of the stabilized crystals^[77]. To achieve in situ synthesis, the lysozyme crystals were pre-immersed in the solvent for three days to ensure fully infiltration of the precursor molecules. In this particular case, the lysozyme crystals were used as macroscopic 3D templates for the confining of ordered arrays of CDs. In another study, Dager et al. also used lysozyme crystals as a matrix to prepare fluorescent CDs-SSL materials^[78]. Different from the *in situ* synthesis reported by England et al., the monodisperse CDs were rapidly synthesized using fenugreek seeds as the carbon source through a one-step microwave plasmon-enhanced decomposition method, and the target product was obtained by a hanging drop method after they were mixed with the lysozyme solution. The fluorescence intensity was relatively uniform throughout the growth of the lysozyme crystals, indicating that the CDs may be evenly dispersed in the crystals.

Recently, we synthesized metal-free phosphors from phthalic acid by one-step heating in formamide solvent (Fig. 3c)^[79]. The phosphor was obtained with a high yield (over 70%) and is composed of single crystals of phthalic anhydride. Interestingly, the crystals could absorb photoluminescent species (Fig. 3d-f), giving the composites yellow or yellow-green emission, with a highest QY of 28.53%.

CDs-SSL materials obtained by crystal encapsulation have high mechanical strength and stability. In general, composites coated with inorganic salts are more stable than those coated with protein crystals. However, due to the wide existence of proteins in living organisms, CDs-SSL materials coated with protein crystals have good biocompatibility and low biotoxicity, which are advantageous over the counterparts coated with inorganic salts.

2.2.2 Surface functionalization

The key of the above-mentioned ways to eliminate ACQ of CDs is to disperse CDs in the crystal/polymer matrix as much as possible. In those cases, CDs can be viewed as solutes while the matrix resembles a solid medium. Utilizing *in situ* or postfunctionalization, groups with large steric hindrances can be introduced on the surfaces of CDs, which can avoid ACQ by forming a barrier and creating a certain distance between adjacent CDs, making the emission more evenly.

2.2.2.1 In-situ-modification

Chen et al. prepared nitrogen-doped CDs which could resist self-quenching by one-pot pyrolysis in water using PVA and ethylenediamine as the carbon and nitrogen sources, respectively^[80]. The surfaces of the obtained CDs were coated with a film formed by chains of PVA, which could produce steric inhibition and create proper space between adjacent CDs in the composites (within the Foster distance). The direct

contact of graphitized carbon nuclei of CDs was thus avoided and the π - π interaction was suppressed, which efficiently inhibited the self-quenching of CDs (Fig. 4a). This study is also the first report to achieve tunable solid-state fluorescence by changing different amines into nitrogen precursors (Fig. 4b). In the subsequent study^[81], the same group induced the moisture resistance, hardening, and oxygen barrier of CDs through modification of PVA chain, and realized the inhibition of self-relief and self-quenching of the aggregated CDs. In another study, Zhu et al. prepared CDs first from CA through a hydrothermal method, which were then subjected to further solvothermal treatment in DMF in the presence of polyvinylpyrrolidone (PVP) and urea^[82]. During the synthesis, the carboxyl groups on the surfaces of the initial CDs were cross-linked with urea through hydrogen bonds. After dehydration and condensation, the initiallyformed CDs grew into larger ones with graphite cores and amorphous surface layers. The chains of PVP on the surfaces of the CDs can protect the triplet state from quenching.

In 2011, Wang et al. Sciences used organosilane as both a solvent and a silanization reagent to synthesize amorphous CDs with surface silanization (abbreviated to be Si-CDs hereafter) for the first time^[83]. Afterwards, Wang et al. prepared a flexible, self-supporting and transparent ionogel by combining CDs and an ionic liquid^[84]. In this case, Si-CDs were first prepared by heating [3(2-aminoethylamino)propyl]trimethoxysilane (AEATMS) and CA. After mixed with [CarbBim]Br, the composite was hydrothermally condensated by a sol-gel method (Fig. 4c). The AE-ATMS-modified CDs were coated with a thin shell formed by oxy-silicon bonds, and imidazole bromide ionic liquid was filled between the surfaces of the CDs and the thin shell. Chen et al. introduced a similar silvlating reagent, N-(β-aminoethyl)-γ-aminopro-



Fig. 4 (a) Schematic illustration of self-quenching-resistance of nitrogen-doped CDs powder, (b) tunable solid-state fluorescence^[80], (c) schematic illustration of the preparation of the CD-ionogel^[84] and (d) schematic diagram of the formation of CDSP through a one-pot sol-gel method^[85]. Reprinted with permission.

pylmethylbimethoxy silane (AEAPMS), to modify CDs. They constructed a double-emission phosphor containing CDs and silica by a sol-gel method with tetraethoxysilane (TEOS) and $Sr_2Si_5N_6$:Eu^{2+[85]}. The surfaces of CDs were wrapped by silica to form a core-shell structure, which further wrap Sr₂Si₅N₆:Eu²⁺ to form a larger core-shell structure (Fig. 4d). Silica could act as a dispersive medium to prevent the aggregation of luminescent nanoparticles and a tie to prevent the separation of the two luminescent substances, imparting the phosphor capabilities of anti-aggregation and anti-phase separation in the matrix. Recently, Sun et al. synthesized CDs by pyrolysis of CA and urea in DMF. After purification, the CDs were further subjected to hydrolysis in DMF in the presence of 3-aminopropyltrimethoxysilane (APTMS)^[37]. During this process, condensation occurred between the surface functional groups of the CDs and APTMS, leading to the formation of SiO₂/CD composite phosphors with CDs embedded in the cross-linked silica network on the surfaces of silica nanoparticles. The QY of the phosphor was considerably high, which was in a range of 30%-60%. The inherent stability of the organosilanes combined with the facile preparation involved in the *in situ*, onestep synthesis makes silanized CDs a promising class of functional nanomaterials.

2.2.2.2 Post-functionalization

The surfaces of CDs were usually distributed a large amount of hydrophilic functional groups, such as hydroxyl, carboxyl, and amino groups, which formed the characteristic surface state of CDs^[86]. These groups can react with a variety of other groups to form covalent bonds, though which task-specific functional molecules can be grafted onto CDs. By using the reverse microemulsion method, You et al. prepared SSL materials by bonding amino-functionalized CDs to cellulose^[87]. TEM images clearly showed that CDs were successfully doped into the cellulose matrix (Fig. 5a-b). It was found that the absorption of the composite increased compared to that of pure cellulose and CDs with the appearance of a wide band at 330-400 nm, indicating that there was not only physical ad-

sorption but also strong interaction between CDs and the cellulose matrix (Fig. 5c). The carboxyl groups of cellulose were dehydrated and condensed with the amino groups on the surfaces of the CDs to form amides. Sakeena et al. prepared highly transparent, nematically ordered hybrid aerogels by modifying amino-functionalized CDs with carboxylated and individualized cellulose nanofibers (*i*-CNF) (Fig. 5d)^[88]. The aqueous carbodiimide coupling between CDs and i-CNF resulted in high QY of CDs and improved properties of the aerogels, including distinctly high specific surface areas and slightly enhanced mechanical strength. This method allows the composites to be equipped with targeted modifiers to meet specific demands. Though it is a bit complicated in processing, but it is more flexible than *in-situ*-modification.

3 Applications of CDs-SSL materials

3.1 WLEDs

Traditional light sources such as incandescent lamps and fluorescent lamps face many problems. The former converts up to 90% of the power into heat, leading to a significantly low power conversion efficiency (PCE). For the latter, the toxic mercury can cause several environmental problems^[89]. Therefore. the search for alternative solid-state lighting sources or devices has aroused extensive research interest. Among them, LEDs, especially WLEDs have attracted wide attention owing to their low power consumption, long lifetime, fast response and high luminous efficiency^[90]. Kido et al. developed the first WLED in 1993^[91]. With the rapid development of material chemistry, it has been possible to prepare organic WLEDs whose pipe fittings are as effective as fluorescent lamps. It is worth noting that CDs-SSL materials with excellent luminescent properties, high stability, and full-color emission have also been applied in WLEDs, which have been demonstrated in many research groups.

According to the standard colorimetric system established by the Commission Internationale De L'Eclairage (CIE) in 1931, the ideal white light emission has a CIE chromaticity coordinate of (0.333,



Fig. 5 (a, b) TEM images with different magnifications of the composite phosphors^[87], (c) absorption spectra of cellulose powder, CDs and cellulose/CDs phosphors^[87] and (d) left: CNF alcogels with coupled CDs under normal light with a laser beam. Right: a schematic illustration showing inter-nanofiber bonds formed upon gel formation and the principle of EDC/NHS-mediated coupling of CDs onto the surfaces of *i*-CNF scaffolds after gelationn^[88]. Reprinted with permission.

0.333). For solid-state lighting, the corresponding color temperature (CCT) is preferably in the range of 2 500-6 000 K, which can be determined by comparing the chroma of the light source with that of an ideal blackbody radiator^[92]. A light source beneficial to human perception should have a high color rendering index (CRI, $R_a > 80$) to reproduce the color of the object^[93]. In the preparation of a WLED, the emission light should cover the whole visible region from 400 to 700 nm. Generally, there are three methods to reach this target, i.e., yellow-light-conversion phosphors (yphosphors) excited by blue-LED (B-LED), three-component (red/green/blue, RGB) phosphors (RGB-phosphors) excited by UV -LED, and single-component white phosphors (w-phosphors) excited by UV-LED^[46].

3.1.1 *y*-phosphors excited by B-LED

A *y*-phosphor excites other colors from blue light and mixes with the remaining unabsorbed blue light to form white light^[94]. The white light created by using two complementary colors, blue and yellow, exists hue isolation, which is usually weak in the red spectrum region and greatly dependent on the forward current. The WLEDs of this type have the characteristics of high correlation color temperature (CCT) and low color display index. In addition, while B-LED is used as the excitation light source, the emitted blue light is harmful to health^[65, 95]. In spite of this, manufacturing WLEDs based on blue-chip and *y*-phosphor is still the most common method^[96].

Through elaborately designed precursors and chemical processes, Li et al. synthesized intercrossed carbon nanorings (IC-CNRs) with relatively pure hydroxyl surface states^[97]. PVA was carbonized rapidly by the hydrothermal method, and the remaining hydroxyl groups on the surfaces formed rings and overlapping each other, finally forming IC-CNRs. The special intercrossed-linking state of the carbon nanomaterials could effectively inhibit ACQ and enabled the emission of stable yellow light in both colloidal and solid states. The IC-CNRs were directly dropped

onto B-LED and dried to form a solid film to prepare WLED with a CIE chromaticity coordinate of (0.28, 0.27). Zhai et al. used CA and urea to synthesize green and red CDs (g/rCDs) through microwave-assisted hydrothermal or DMF solvothermal synthesis, which were dispersed in starch/PVP to obtain composite phosphors with good light stability and structural stability. The phosphors were further combined with blue InGaN chip to obtain WLEDs^[98]. The blue emission of the chip first excited the gCDs@starch phosphor to emit green light and then excited the rCDs@PVP phosphor to produce red light (Fig. 15). The CRI of the obtained WLED was as high as 92, and the CIE chromaticity coordinate was (0.33, 0.33). In a recent study, Wang et al. prepared WLEDs by using oil-soluble yellow-green luminescent CDs prefrom acetone and dimethyltrithiocarbon pared (DMTTC) and GaN blue chip (Fig. 6a)^[99]. A typical device had a CIE chromaticity coordinate of (0.33, 0.30), a CCT of 5 389 K, and a CRI of 88.38. 3.1.2 RGB-phosphors excited by UV-LED

In practical applications, small stokes shift between different components may lead to heavy reabsorption of the emission and fluorescence resonance energy transfer, which labilizes the light color and decreases the luminous efficiency^[51, 95]. In addition, some kinds of phosphors themselves undergo attenuation of brightness and decrease of the optical stability, which could also lead to color migration and self-quenching^[65]. However, compared to B-LEDs, the emission of UV-LED is independent of the white light emitted by the mixed phosphor, which can provide higher energy^[100]. Besides, the emission spectra of the RGB-phosphors exhibit a great overlap, which is conducive to the preparation of WLEDs with high CRI and high efficiency. By adjusting the ratio of the three kinds of phosphors, high CRI can be maintained while the CCT is changed.

Sun et al. obtained blue-CDs by hydrothermal treatment of CA and ethylenediamine, and red/green PDs by ultrasonic treatment of the mixed solution of PFTBT/PF10BT and PSMA (Fig. 6b). After that, they added these three kinds of luminescent materials to silica gel and solidified them on a UV-LED chip to obtain a WLED^[51]. All of the three luminaries in the WLED had the characteristics of weak reabsorption, no energy transfer crosstalk, and wider half-width modulation, which gives the as-prepared WLED high CRI and high efficiency. When the forward current was increased from 10 to 50 mA, the CIE chromati-



Fig. 6 (a) Construction and characterization of the WLEDs based on oil-soluble yellow-green luminescent CDs: (a₁) structural diagram, (a₂) CIE color co-ordinates, (a₃) lighting photo, and (a₄) emission spectrum with upper right inset showing a real photo of the WLED lamp^[99], (b) images of CD/PVP,
 PF10BT/PVP and PFTBT/PVP powder (b₁) under daylight and UV light, and (b₂) true-color images of WLEDs in different ratios of phosphors^[51] and (c) the assembly of the LED device (c₁), and (c₂) emission spectrum of the LED^[107]. Reprinted with permission.

city coordinate of the WLED only changed from (0.324, 0.344) to (0.326, 0.343) and the CCT changed from 5 843 to 5 750 K. The small changes confirmed the stability of the color. Tian et al. prepared RGB-CDs using CA and urea as raw materials by hydro-thermal/solvothermal treatment in different solvents and solvent combinations (water/glycerol/DMF)^[101]. CDs were dispersed in sodium silicate and then covered on an InGaN chip to prepare a WLED. When the ratio of the RGB-phosphors was 10 : 10 : 1, a pure WLED with a CIE chromaticity coordinate of (0.32, 0.33), a CCT of 6 109 K, a CRI of 88 and a luminous efficiency of 6.3 lm·W⁻¹ was obtained. 3.1.3 *w*-phosphor excited by UV-LED

Based on the use of high-energy UV-LED chips, the selection of single-component phosphors for the preparation of WLEDs is usually characterized by non-fading, non-phase separation and simple device manufacturing process over time^[38]. In addition, tuning the mixing ratio of various phosphors, as encountered in RGB-based WLEDs, is avoided^[95]. Due to the fundamental limitations imposed by the Kasha rule (for molecules with multiple states, photons can only be emitted from the lowest excited state), the development of highly emissive, single-component WLEDs generated by double emission is a great challenge^[102]. Although rare-earth-based phosphors and inorganic semiconductor QDs possess strong absorption and emission that can be effectively applied in the preparation of single-component WLEDs, most of them require dopants of metal ion with non-intrinsic red emission or surface defect states to supplement the red spectral region, which inevitably leads to low CRI^[103]. In recent years, the unique wide emission of fluorescent CDs has enabled them to be used in single-component WLEDs, making them ideal materials for optoelectronic applications^[38, 104–106].

By using CA as a carbon source and L-cysteine as an additive, Wang et al. synthesized nitrogen-sulfur co-doped CDs (NS-CDs) through a simple hydrothermal method and prepared a WLED emitting warm white light using 365 nm UV-LED by dispersing NS-CDs in PVA^[53]. The WLED has a CIE chromaticity coordinate of (0.40, 0.38), a CCT of 3 980 K, and a brightness of 3 629 $\text{CD}\cdot\text{m}^{-2}$. Joseph et al. prepared white light-emitting CDs by carbonizing ethylene diamine tetra acetic acid (EDTA) and ethylene glycol (EG). The various functional groups in the precursors produced inhomogeneity on the surfaces of the CDs^[57]. Using the remote phosphor technology, the CDs were dispersed in PMMA and covered on a 365 nm UV chip to realize white light emission. The results showed that the CIE chromaticity coordinate of the prepared WLED is (0.34, 0.38), CRI is 84, and CCT is 5 078 K. By using ammonium citrate and phosphate as a carbon source and an additive, Zhang et al. synthesized nitrogen and phosphorus co-doped CDs (TAP-CDs) with satisfying optical and thermal properties through one-step rapid microwave assisted synthesis^[100]. Singe-component WLED was prepared by using TAP-CDs as the phosphor, which was mixed with an optically transparent adhesive and coated on the LED lens. The emission spectrum of the prepared bright-warm-emitting WLED almost covered to the entire visible range (400-700 nm), of which the CIE chromaticity coordinate is (0.38, 0.35) and the CCT is 4 450 K. In a recent study, Gu et al used the solidphase microwave-assisted (SPMA) technology to synthesize highly fluorescent nitrogen-doped GQDs (NGQDs) and graphitic carbon nitride quantum dots (CNODs). Independently luminescent films were prepared using silica gel as the matrix^[107]. The LED prepared by the luminous film can emit white light, with a CIE chromaticity coordinate of (0.35, 0.36) (Fig. 6c). The stability and durability of the device were further investigated. It could be concluded that the emission intensity, CRI and QY were relatively stable with the change of current, and the device had excellent stability over time.

3.2 Optical sensors

3.2.1 Temperature sensors

Temperature plays a critical role in various functions and reactions^[108, 109]. With the increase of the demands for temperature monitoring, the traditional intrusive/contact methods, such as thermistors and thermocouples, are gradually unable to meet the requirements, leading to the development of non-invasive nanothermometers^[110]. In the selection of nanoscale temperature measurement using different properties, the fluorescence system with spatial resolution and high temporal can mostly stimulate the research interest.

Wang et al synthesized two kinds of CDs with opposite charges from CA and urea and prepared double-emission fluorescent nanospheres by electrostatic self-assembly^[111]. The nanospheres had a strong reversible response to external temperature driven by the change of the surface states of CDs. Their fluorescence intensity changed with the variation of external temperature (Fig. 7a, b). The reversible change of fluorescence color of the nanometer thermometer can realize the visual detection of temperature and be available for optical temperature measurement with high reproducibility (Fig. 7c). In the follow-up study, this research group assisted the self-assembly of CDs under the same conditions with pre-prepared polystyrene (PS) nanoparticles to obtain solid *w*-phosphors^[89]. The phosphors exhibited reversible, temperature-dependent fluorescence controlled by surface functional groups. Jiang et al. prepared PU/CD composite films with double emission properties^[112]. As the ambient temperature was increased, the green-yellow emission of the film gradually decreased, while the blue emission of the PU film itself remained unchanged, making the color of the film changed from yellow-green to blue in the macroscopically visible range (Fig. 7d).

Li et al. prepared CDs-grafted CaAl₁₂O₁₉:Mn⁴⁺ (CaO) hybrid phosphors by a facile one-step sol-gel method^[113]. The obtained CD/CaO phosphors had temperature-dependent luminescent properties and could be used for temperature sensing in a wide linear



Fig. 7 (a) Fluorescence spectra with increasing temperature from 15 to 85 °C or (b) decreasing temperature from 85 to 15 °C, (c) eight cycles of intensity variations measured at 15–85 °C^[111], (d) fluorescence images of films with increasing the temperature from 10 to 90 °C^[112], (e) fluorescence intensity of the functional PVA film as a function of the oxygen concentrations for the emission centers of 310 nm, (f) reversibility of the functional PVA film for each emission center during three consecutive 0–21 kPa O₂ cycles^[120] and (g) emission spectra of CDs-PSi measured at different oxygen volume fractions (λ_w=366 nm)^[123]. Reprinted with permission.

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range of 80–300 K. In this direction, Wang et al. prepared a flexible isotropic thin film by a core-shell method using cellulose nanocrystal (CNC)-assisted, CDs-grafted $SrAl_2O_4$, Eu^{2+} , Dy^{3+} (SAO)^[114]. The luminescence of the thin film was very sensitive to the ambient temperature (243–383 K) and has good linear properties.

3.2.2 Oxygen sensors

Monitoring the level of molecular oxygen is essential in biological detection, environmental monitoring, chemical analysis, aerodynamics and food packaging^[115]. The sensors generated by photosensitization of specific organic ligands coordinated with heavy metal ions, such as Pd(II), Pt(II), or Ru(II), can effectively realize reversible and non-destructive oxygen sensing^[116-119]. Unfortunately, the costs of this class of sensors are too high in practical applications, which limits their large-scale production^[120]. The introduction of optical sensing into oxygen-monitoringsystem gradually attracted the attention of researchers. The ratiometric fluorescence method can be used to detect the concentration of oxygen by measuring the change of photoluminescent intensity caused by the energy transfer of oxygen-sensitive light emitters. Generally, phosphorescent materials with long excitation lifetime are more suitable for the preparation of oxvgen sensors^[121].

Using KH-602 and anhydrous CA as precursors, Lei et al. synthesized CDs by a hydrothermal method and assembled them into ordered pores of a mesoporous material (SBA-15) obtained from P-123 and ethyl orthosilicate to obtain a CD/SBA-15 hvbrid material^[122]. The CD/SBA-15 had invertible oxygen sensing signal and well photochemical stability. Its fluorescent intensity decreased significantly with increasing the concentration of oxygen, and the response time was relatively short (about 7-10 s). At the same time, the selectivity of this hybrid material to oxygen was obviously higher than that of other gases, so it could be used for detecting oxygen in a large range or even very low concentration. In the study performed by Tan et al., isophorone diisocyanate (IP-DI) was used as the single carbon source to synthess

nitrogen-doped CDs under microwave irradiation. which were further dispersed in the polyurethane matrix to obtain oxygen-sensitive CQD/PU composites^[61]. After the CQD/PU composites were placed in a nitrogen atmosphere and air for 48 h and irradiated by UV for 5 min, it was found that the intensity of phosphorescence nearly unchanged under the nitrigen atmosphere, while quite opposite in air. Under nitrogen purging for 12 h, the significantly decreased intensity of phosphorescence of the sample-in-air was recovered. The oxygen sensitivity of CQD/PU composites under UV excitation can be used for novel oxygen sensors. Armegan et al. integrated the hydrothermal products of urea and p-phenylenediamine into a PVA matrix to prepare a multi-emission oxygen sensor that could realize reversible oxygen sensing^[120]. The 2D fluorescence contour plots of the prepared multi-emission fluorescent materials showed that the three emission centers underwent oxygen induced ACQ at 0, 1, 2, 4, 8 and 21 kPa O₂, and the quenching followed the nonlinear Stern-volmer curve (Fig. 7e). The oxygen sensor showed reversibility during three cycles (Fig. 7f). Wang et al. prepared a fast, selective and highly sensitive oxygen sensor based on CDs which were grafted to $CaSiO_3 : Eu^{3+[123]}$. While Ca- SiO_3 : Eu³⁺ itself was less affected by oxygen, the composite grafted with CDs had good oxygen sensitivity (Fig. 7g). Both the red emission of Eu^{3+} and the blue emission of CDs were effectively reduced with increasing the concentration of oxygen. The response time was among 4-7 s and the recovery time was 18-29 s.

3.2.3 Pressure sensors

Except for temperature and composition, pressure is the thermodynamic variable which can effectively affect the electronic structure, atomic arrangement and molecular interaction of materials. With the rocket like development of high-pressure technology, particularly the application of the diamond anvil cell (DAC), the research of the high-pressure field has been carried out extensively^[124–127]. Thus, pressure-responsive luminescent materials used to detect pressure changes have aroused considerable concern due to their wide range of potential applications^[59, 128]. Mechanical fluorescent materials can change their photoluminescent color in response to mechanical stimulation, but traditional mechanical fluorescent materials can only change their photoluminescent color in one direction.

By chemically and purposefully controlling the content of carbonyl groups and π -electron systems, Liu et al. reported blue-shift and red-shift CDs triggered by controlled pressure^[125]. The carbonyl groups and conjugated systems contained in CDs play a key role in the photoluminescence of CDs under high pressure. The increase of pressure enhanced the π - π accumulation of the π -conjugated system and further leads to the red shift of photoluminescence, oppositely the conversion of the carbonyl group eventually leads to the blue shift. Under high pressure, the structure of most CDs was destroyed and led to ACQ. Wang et al. first reported the synthesis of pressuretriggered aggregation-induced emission of red CDs (R-CDs) obtained by a solvothermal method using 1,3,5-benzenetrithiol as a precursor^[59]. The aromatic rings contained in R-CDs are cross-linked by weak interactions, which oscillate dynamically within the crown and consume energy in the non-radiative decay pathway. The confinement provided by pressure could limit the oscillations within the particles, thus blocking the non-radiating channels and opening the radiating channels, resulting in obvious photoluminescence enhancement of R-CDs. The R-CDs were further developed into pressure sensitive materials by combining with PDMS.

4 Conclusion and outlook

In this review, we have emphasized the recent progress in CDs-SSL materials in terms of their synthesis and applications in WLED and optical sensors. In recent years, different methods have been developed to solve ACQ during the preparation of CDs-SSL materials and great progress has been made. Related studies have promoted the applications of CDs from solution state transferring to solid state, bringing them closer to the multifunctional material. In terms of physically-doped CDs in solid matrices, most of the substrates currently used are polymers, with a small number of reports used inorganic crystals, both of them are easy to process, cheap and easily available. In practice, CDs are structurally similar to proteins, and have great biocompatibility. The composite materials produced by the combination of CDs and proteins have broad potential applications in life science and related fields. However, there are few relevant studies at present. On one hand, many familiar organic chemical reactions have not yet been used to modify the surface of existing CDs. On the other hand, in the post-modification process, the mechanism behind the change of photoluminescence for CDs also needs to be further elucidated.

Previous studies have shown that CDs-SSL materials have a wide scope of applications, including WLEDs and sensing, which has been specially emphasized in this review. Benefit by the emission tunability of CDs (dependent on various factors, like pH, particle size, surface state), the CDs-SSL materials with full-color emission could be successfully obtained. Generally, with the retained optical properties and biological affinity properties of CDs, the CDs-SSL materials have significant advantages over traditional materials widely used in WLEDs and optical sensing fields. Nevertheless, relying solely on the advantages originating from CDs may also hinder further exploration of the unique properties of CDS-SSL materials themselves. In the field of visual fluorescence sensing, current applications of CDs-SSL materials largely depend on the CDs contained inside. Using the physical and/or chemical interactions between CDs and substrates to construct composites with specific environmental dependence and fluorescence reversibility will be able to go beyond the constraints of CDs and further expand the applications of such materials in this direction.

Although CDs-SSL materials still face some challenges, we believe that with the cooperation of scientists from different fields, CDs-SSL materials will definitely show strong vitality in more fields, and this fascinating class of nanoscale luminescent materials will undoubtedly attract more and more researchers to join in.

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基于碳点的固体发光材料:合成及其在白光发射二极管和 光学传感器中的应用

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摘 要: 碳点已成为碳质纳米材料家族的一颗新星。自从它们于 2004 年被偶然发现以来,获得了广泛的研究。基于碳点 的固态发光材料环境友好、无毒、廉价,是取代稀土发光材料和半导体量子点的理想选择。然而,由于碳点易表现出聚集 诱导猝灭的特点,将它们从溶液态转入固态时,如何保持其发光特性是一大挑战。本文介绍了碳点的合成方法,碳点基固 态发光材料的制备方法及其在白光发光二极管和光学传感器中的典型应用。最后指出了碳点基固态发光材料仍然存在的缺 点,并对其在白光发射二极管和光学传感器和其它领域的发展前景进行了展望。

关键词: 碳点; 纳米材料; 发光; 白光发射二极管; 光学传感器

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