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Original
Fluorescent carbon dots in solid-state: From nanostructures to functional devices / Ren, J.; Stagi, L.; Innocenzi, P.. - In: PROGRESS IN SOLID STATE CHEMISTRY. - ISSN 0079-6786. - 62:(2021), p. 100295. [10.1016/j.progsolidstchem.2020.100295]

Availability:
This version is available at: 11388/240697 since: 2022-04-16T12:55:34Z

Publisher:

Published
DOI:10.1016/j.progsolidstchem.2020.100295

Progress in Solid State Chemistry xxx (xxxx) xxx

Contents lists available at ScienceDirect

Progress in Solid State Chemistry

journal homepage: www.elsevier.com/locate/pssc

Fluorescent carbon dots in solid-state: From nanostructures to functional devices

Junkai Ren, Luigi Stagi, Plinio Innocenzi *

Laboratory of Materials Science and Nanotechnology (LMNT), Department of Chemistry and Pharmacy, University of Sassari, CR-INSTM, Via Vienna, 2, 07100, Sassari, Italy

ARTICLE INFO

Keywords:
Carbon dots
Sensing
Photonics
Hybrid organic-inorganic materials
Nanocomposites

ABSTRACT

In recent years, carbon dots (CDs) have attracted considerable attention for their potential application in photonics and optoelectronics. One of the main limitations in realizing efficient and reliable solid-state devices is the aggregation-caused quenching effect. At a short distance, the mutual interaction among nanoparticles enhances the non-radiative mechanisms, undermining the extraordinary optical properties of CDs. In this review, we have critically analyzed the main strategies for maintaining and empowering the optical properties of CDs from liquid to solid-state. These routes include the preparation of self-quenching-resistant fluorescent CDs and the embedding into different matrices. The material processing and the nature of the chemical environment surrounding the CDs are key parameters for selecting an optically transparent matrix. An optimized host material would preserve the fundamental properties of CDs, but also improve their performances extending the application field. Many types of matrices for CDs have been tested, such as polymers, organic-inorganic hybrid materials, mesoporous and layered materials. Besides, unconventional host materials have also used as a matrix, e.g. acid molecules condensates and inorganic salts. The successful use of CDs is highly relying on their incorporation into a solid-state matrix.

1. Introduction

Since their discovery in 2004 [1,2], an increasing effort has been devoted to disclosing the mechanisms governing the optical properties of carbon dots (CDs). Compared with traditional fluorescent materials, CDs possess various advantages, such as low production cost, facile and environment-friendly preparations, tunable photoluminescence (PL), high quantum yields (QYs), excellent stability and good biocompatibility [3–6]. The outstanding CD properties disclose new possibilities in bioimaging and biotherapy, lighting and display, laser and optical limiting, photocatalysis and fluorescent sensing [7–10].

The successful exploitation of the CD properties, except for CDs dispersed in solutions used for applications in biotechnologies and sensing, is largely relying on the appropriate integration into a solid-state device. In general, the direct incorporation of CDs into a host matrix would lead to some negative effects, such as the decreasing of transmittance due to Rayleigh scattering, the fluorescent quenching caused by aggregation and the phase separation. In some cases, the low doping concentration represents the main issue because of CD low solubility or difficult dispersion [11,12]. Hence, it is an important task to achieve an efficient dispersion of CDs into solid-state matrices, maintaining at the same time an excellent performance of the device.

The aggregation-caused quenching (ACQ) phenomenon is usually described as a strong luminescent loss or quenching of fluorophores occurring at high-concentration solutions or in solid-state. Luminescent molecules can undergo fluorescent quenching as a result of non-radiative contribution arising from mutual interactions (mainly π–π interactions) [13]. As for the aromatic hydrocarbons, CD emission shows a marked ACQ effect caused by photon reabsorption and non-radiative energy transfer in solid-state. Because of the complex structure of CDs, the mechanism of quenching can be multiple and difficult to identify. For instance, CDs can be interested in both static and dynamic quenching right after the formation of nonfluorescent ground-state complexes or as a result of charge or energy transfer between functional groups at the CD surfaces. The former can be characterized by a change in the absorption spectrum while the fluorescence lifetime does not change with the concentration [14]. The latter is strongly dependent on the concentration due to the corresponding increase of CD collisions and it is typically identified by the Stern-Volmer relation [14].

ACQ effect not only leads to the complete PL quenching of CDs in

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* Corresponding author.
E-mail address: plinio@uniss.it (P. Innocenzi).

https://doi.org/10.1016/j.progsolidstchem.2020.100295

Please cite this article as: Junkai Ren, *Progress in Solid State Chemistry*, https://doi.org/10.1016/j.progsolidstchem.2020.100295

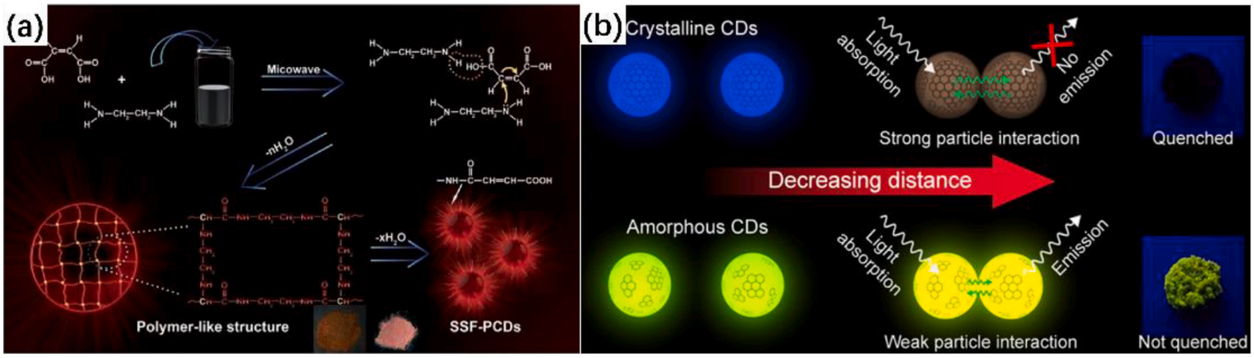

Fig. 1. Some mechanisms for self-quenching-resistant emissive CDs in solid state: (a) cross-linked structure [15], and (b) amorphous surface state [18]. (a) Reprinted with permission from Ref. [15]. Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany. (b) Reprinted with permission from Ref. [18]. Copyright 2019, American Chemical Society.

solid-state matrices but also can contribute to a severe modification of spectral features. ACQ control represents, therefore, one of the main tasks to get the required CDs loading into solid-state matrices without losing the spectral characteristics and performances of CDs.

Currently, CDs have been incorporated into solid-state devices using two main strategies: (i) the synthesis of self-quenching-resistant solid-state fluorescent CDs [15–29], and (ii) the embedding of CDs into a solid-state matrix, including polymers [30–84] and hybrid organic-inorganic sol-gel materials [85–110]. CDs incorporation in matrices can be further divided into simple-physical dispersion and copolymerization. Moreover, mesoporous [111–116] and 2D layered materials [117–119] have been developed as host matrices to fabricate optical devices based on CDs. Besides, some acid molecules [120,121], inorganic salts [122–124], and metal oxides [125–127] have also been used to employ CDs as solid-state emitters. The use of host matrices can both preserve CD optical responses and empower their luminescent properties.

In this article, we have reviewed the main methods to process CDs at solid-state. The corresponding advantages are also summarized, with particular attention on the strategies to boost the fluorescent properties.

2. Self-Quenching-resistant CDs

As a consequence of particle aggregation, we assist to a significant decrease in CDs fluorescence, making them useless in solid-state applications. Therefore, it appears of primary importance developing new types of CDs with anti-self-quenching properties. There are many reports about self-quenching-resistant CDs [15–29]. Herein, we mainly concentrate on the preparations and possible mechanisms governing this type of carbon nanoparticles.

Development of cross-linked structures is one of the most popular ways for the realization of CDs with quenching-resistant solid-state emission [15–17]. As shown in Fig. 1a, CDs with a cross-linked structure can be synthesized by maleic acid and ethylenediamine through microwave treatment [15]. It has been observed that during the carbonization process a net structure is formed around the CD core, which prevents quenching of the emissive centers by nanoparticle proximity interactions.

The surface state is considered as the key factor for the realization of quenching-resistant fluorescent CDs [18,19]. CD self-quenching issue is related to the content of sp^2 domains in the nanoparticles [18]. Indeed, amorphous CDs, prepared by a short carbonization treatment, show strong emission in powder state. Crystalline CDs, with a higher sp^2 domain content, instead, tend to lose much of the fluorescence due to strong particle interaction (Fig. 1b).

Additionally, Meng et al. [20] have designed CDs systems by solvothermal treatment of guanidine carbonate and monopotassium phosphate. The resulting structures displayed both quenching-resistant properties through the formation of hydrogen bonds and broad-band emission. This approach also allows realizing tunable solid-state

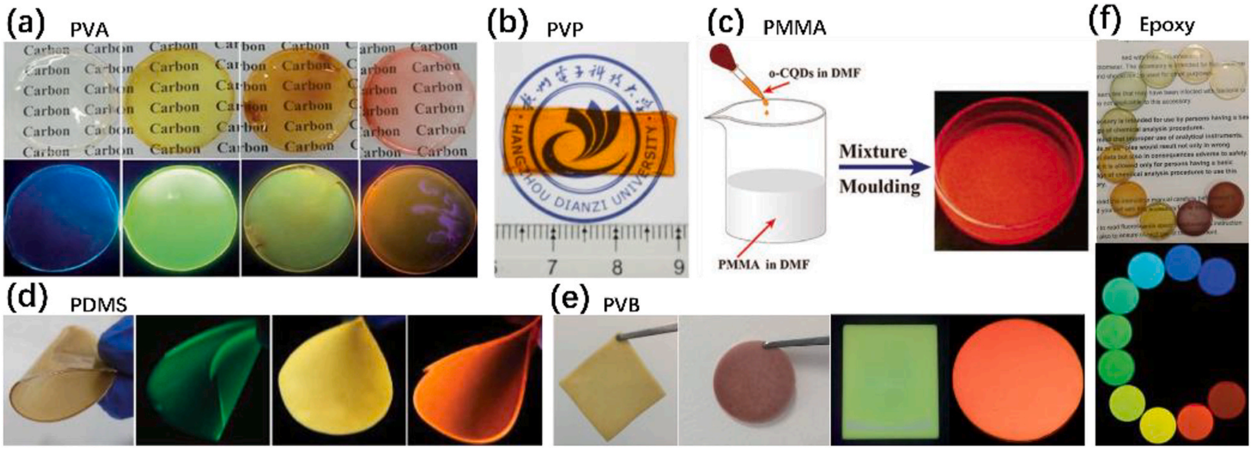

Fig. 2. Some CDs-polymer composites by physical dispersion: (a) PVA [30], (b) PVP [39], (c) PMMA [44], (d) PDMS [48], (e) PVB [51], and (f) epoxy [54]. (a) Reprinted with permission from Ref. [30]. Copyright 2019, Royal Society of Chemistry. (b) Reprinted with permission from Ref. [39]. Copyright 2017, American Chemical Society. (c) Reprinted with permission from Ref. [44]. Copyright 2017, Royal Society of Chemistry. (d) Reprinted with permission from Ref. [48]. Copyright 2016, Royal Society of Chemistry. (e) Reprinted with permission from Refs. [51]. Copyright 2015, Royal Society of Chemistry. (f) Reprinted with permission from Ref. [54]. Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

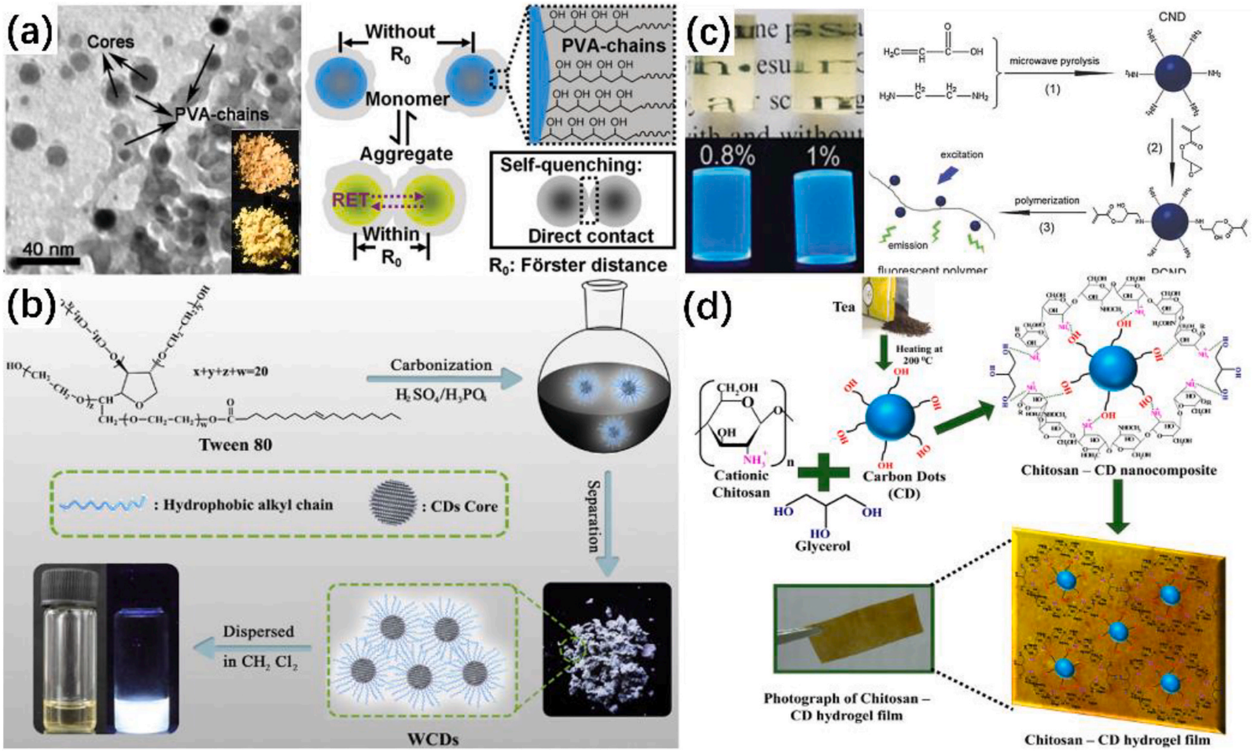

Fig. 3. Polymer-functionalized CDs: (a) CDs synthesized from PVA [64], (b) CDs synthesized from Tween 80 [65], (c) Vinyl-functionalized polymerizable CDs [70], and (d) Chitosan-CDs nanocomposite hydrogel film [72]. (a) Reprinted with permission from Ref. [64]. Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany. (b) Reprinted with permission from Refs. [65]. Copyright 2017, Elsevier Ltd. (c) Reprinted with permission from Ref. [70]. Copyright 2012, Royal Society of Chemistry. (d) Reprinted with permission from Ref. [72]. Copyright 2014, Elsevier Ltd.

emitters as shown by Shen and co-workers [21], who have developed an effective solvothermal route to embed CDs into trisodium citrate crystal, showing tunable solid-state emission. As the authors describe, the CDs are also self-quenching-resistant.

3. CDs in polymeric materials

Presently, incorporation of nanomaterials in a polymer matrix to maintain their intrinsic properties and extend the fields of application, is a common procedure. Depending on the polymer properties a large variety of CD composites can be designed and fabricated, including flexible films. Moreover, the host materials can also boost the CD properties. The methods can be divided into two main routes: (i) Physical dispersion, and (ii) Chemical copolymerization.

3.1. Physical dispersion of CDs in polymer materials

A CD-polymer structure can be fabricated via two simple steps: (i) dissolution of the polymer in an organic solvent together with the CDs; (ii) the CDs-polymer composite is molded by removing the solvent. Different types of polymers have been used as CD matrices (see Fig. 2), such as polyvinyl alcohol (PVA) [30–38], polyvinylpyrrolidone (PVP) [39–43], poly(methyl methacrylate) (PMMA) [44–47], polydimethylsiloxane (PDMS) [48–50], polyvinyl butyral (PVB) [51–53], epoxy [54,55], polyethylene glycol (PEG) [56,57], and polyurethane (PU) [58,59]. Dispersion in polymeric matrices can lead to significant advantages in terms of optical properties. When embedded in matrices in rigid positions, non-radiative interactions between CDs are significantly reduced, avoiding the inconvenience of ACQ. However, this effect applies to a defined range of concentrations and depends on the characteristics of the CDs (*vide infra*). Furthermore, the choice of the host polymer is of primary importance both to preserve the QY and fit the application requirements. For example, PMMA can be used to fabricate fluorescent plexiglass [44] and freestanding films [47] by incorporation of CDs.

Additionally, some natural polymers (e.g. cellulose [60–62] and starch [63]) have also been used as matrices for CDs. Indeed, the abundant carboxyl groups of cellulose can covalently and electrostatically attach to amino groups of CDs, which favours the uniform dispersion of CDs in cellulose films [60].

As the concentration of CD in the polymers increases, the intensity of the fluorescence generally first shows an increase for a significant loading interval and then gradually decreases [36,52]. The enhanced PL in the first stage is due to the rising number of phosphors with weak mutual interactions and, correspondingly, a high QY. The PL loss in the second stage results from the ACQ effect. Moreover, the increase of concentration can lead to the emissive color change in CDs-polymer composites. For example, Zhang et al. [50] prepared CDs that showed a red-shift from 435 to 550 nm in solution when the concentration changed from 0.2 to 1000 mg mL^{-1}. After dispersing in PDMS, the red-shift has still been observed from their solid-state emission. Subsequently, the authors have been able to tune the electroluminescence spectra of the fabricated White LEDs (WLEDs) from cold to warm white light region by dispersing the CDs in PDMS and increasing the CDs concentration.

3.2. Polymer-functionalized CDs

For maximizing CD optical properties in matrices, organic prefunctionalization has proved an effective method. Polymers are also widely used as precursors to synthesize CDs with a cross-linked chain taking advantage of their macromolecular structure [64–69]. As shown in Fig. 3a, Chen et al. [64] have used PVA and ethylenediamine as precursors to prepare CDs by hydrothermal method. The obtained CDs consisted of long PVA-chains around the surface preventing the emissive centers from approaching each other. Interestingly, the authors have

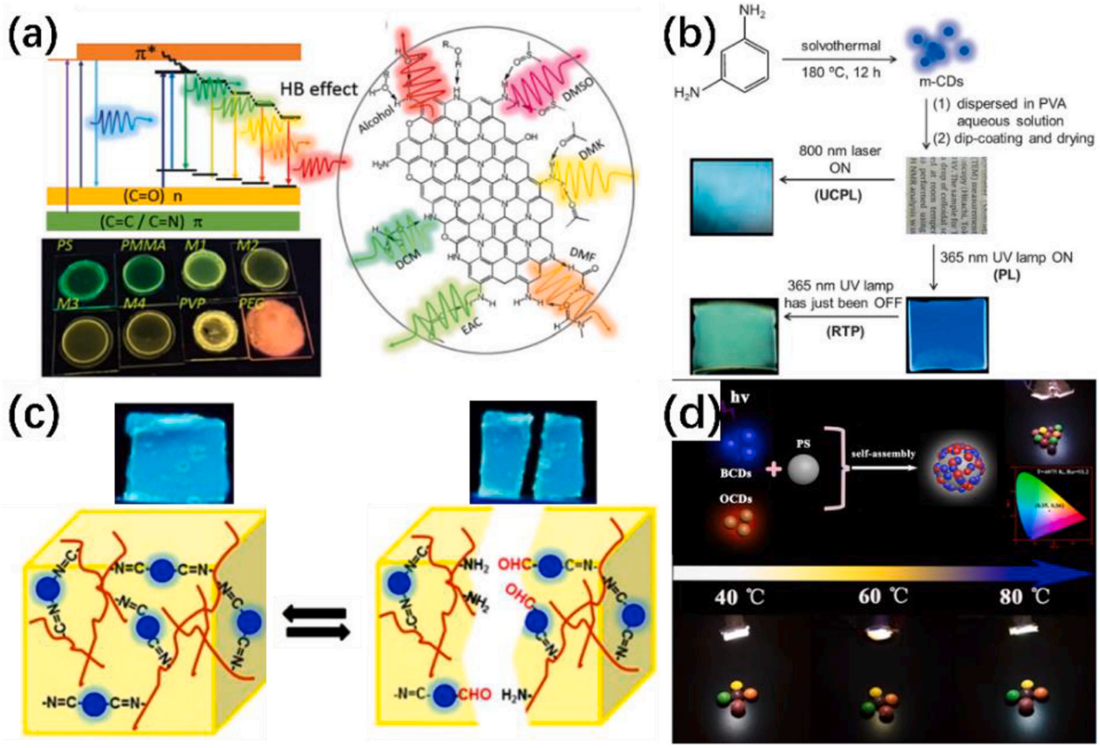

Fig. 4. Optical properties of CDs in polymer matrices: (a) Solvatochromism of CDs in different polymer matrices [73], (b) Room temperature phosphorescence from CDs-PVP composite [77], (c) Fluorescent self-healing CDs-PEI gels [80], and (d) Temperature-dependent LEDs based on CDs-PS composite [83]. (a) Reprinted with permission from Ref. [73]. Copyright 2017, Royal Society of Chemistry. (b) Reprinted with permission from Ref. [77]. Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany. (c) Reprinted with permission from Refs. [80]. Copyright 2019, American Chemical Society. (d) Reprinted with permission from Ref. [83]. Copyright 2019, American Chemical Society.

achieved a high tunability of the optical properties using this route, demonstrating the application of CDs for white-emission LED. Jiang and co-workers [65] have prepared a type of white-emissive CDs with long alkyl-chain structure by carbonization of Tween 80 under sulfuric acid and phosphoric acid (Fig. 3b). In this case, the white CDs can be used for both white-LEDs and latent fingerprints imaging.

To improve the compatibility of the CDs in polymers, it is necessary to functionalize them by specific organic molecules [70–72]. Zhang et al. [70] have prepared CDs with amine surface groups through microwave treatment of acrylic acid and ethylenediamine, allowing further reaction with glycidyl methacrylate to synthesize vinyl-functionalized polymerizable CDs (see Fig. 3c). The resulted CDs can co-polymerize with methyl methacrylate, which guarantees a uniform dispersion of the nanodots in a PMMA matrix. This approach can also improve the mechanical properties of the composite. As an example, Konwar and co-workers [72] have synthesized CDs from tea, allowing the hydroxyl groups of CD surface to interact electrostatically with the NH_3^+ groups of chitosan (Fig. 3d). The corresponding chitosan-CD nanocomposite films have an improved mechanical strength with a remarkable rise of the tensile strength value from 5.057 to 18.595 MPa.

3.3. *Empowered properties from CD-polymer composites*

The proper polymeric matrices-CDs combination increases the fluorescence efficiency and, more in general, the composite performances. As for many molecular compounds, it is frequently observed in CDs solutions a color modification depending on the solvent, namely solvatochromism. This effect can also be detected when CDs are dispersed into solid-state matrices [73–76]. For instance, Zhang et al. [73] have prepared CDs from *p*-phenylenediamine via solvothermal route, coupled with molecular state fluorescent mechanism. When the CDs are dispersed into different solvents, the emission shows a strong shift from 540 to 614 nm (540 nm in chloroform, 559 nm in acetone, 590 nm in dimethylsulfoxide). This phenomenon is also observed in CD-polymer composites. Fig. 4a shows that the emission is red-shifted from the green to the red region when the dots are incorporated into PS, PMMA, PVP, and PEG polymers, respectively.

The possibility to exploit the phosphorescence from CDs at room temperature for specific applications, has aroused wide interest from researchers. Several CDs displaying a strong fluorescence in solution, exhibit phosphorescence in polymeric matrices [77–79]. As shown in Fig. 4b, the CDs synthesized by solvothermal treatment of *m*-phenylenediamine, possess 6.41 ns of fluorescence lifetime in ethanol, and a component with 456 ms phosphorescent lifetime in a PVA film [77]. According to the authors, the hydroxyl groups in PVA form hydrogen bonds with C–N/C=N groups of the as-prepared CDs, with a resulting three-component emission of CDs incorporated into the polymeric matrix. Furthermore, as a good oxygen barrier, PVA can prevent oxygen from quenching phosphorescence.

CDs have also been tested in self-healing gels, which have the intrinsic ability to repair after damage. It has turned out that the composites manifested improved mechanical strength and multicolor fluorescence, at the same time [80–82]. Bhattacharya and co-workers [80] designed fluorescent self-healing gels by the reaction between CDs synthesized from aldehyde precursors and branched polyethyleneimine (PEI) (see Fig. 4c). Strain sweep experiments have shown that the imine-bond network between CDs and PEI can contribute to improving the mechanical strength and resilience of the self-healing gels. Furthermore, it has been proved that CDs can also enhance the self-healing process.

Temperature-dependent emission has been investigated in CDs-polymer systems [83,84]. Fig. 4d shows the mechanism of CDs-PS phosphors as a function of temperature [83]. The emitting spectrum can be tuned from white (emission, ~ 400–730 nm) to blue light

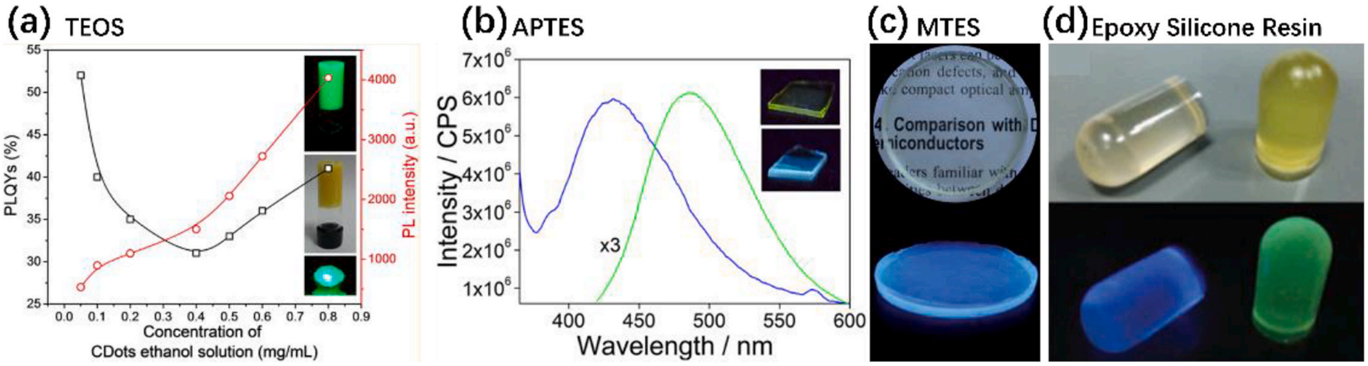

Fig. 5. Some CDs-hybrid organic-inorganic nanocomposites obtained by physical dispersion: (a) CDs/TEOS-gel composites [85], (b) CDs/APTES-gel composites [88], (c) CDs/MTES-gel composites [90], and (d) CDs/epoxy silicone resin composites [92]. (a) Reprinted with permission from Refs. [85]. Copyright 2017, American Chemical Society. (b) Reprinted with permission from Refs. [88]. Copyright 2020, Springer Nature. (c) Reprinted with permission from Refs. [90]. Copyright 2014, Royal Society of Chemistry. (d) Reprinted with permission from Ref. [92]. Copyright 2014, Royal Society of Chemistry.

(emission, ~ 440 nm) in a 20–80 °C range, opening potential applications as novel LED-sensors of temperature.

4. CDs in hybrid organic-inorganic sol-gel materials

Sol-gel processing [128] is particularly effective to obtain tailored hybrid organic-inorganic matrices for CDs. A common route to incorporate the CDs into an organic-inorganic hybrid matrix via sol-gel starts by dissolving the precursors in alcoholic solvents, which are good solvents for CDs. On the contrary, the incorporation of CDs in a polymer matrix may require a specific solvent to dissolve the polymer and CDs at the same time. Another advantage of sol-gel synthesis is the high chemical and thermal stability of the derived hybrids that usually surpasses that of the most common polymers in harsh conditions, e.g. high temperature and UV radiation.

Sol-gel chemistry turns out to be highly flexible for functional applications. Organically modified alkoxides, e.g. methyltriethoxysilane (MTES), are characterized by a Si–C functional group, which does not hydrolyze during the sol-gel reactions. This allows fabricating hybrid materials whose properties are governed by the precursor choice with a special organic functional group. The proper design of the host hybrid is used to enhance the guest CD properties. The main strategy to incorporate CDs in the hybrid material is the dispersion of CDs in the precursor sol; the sol is then used to fabricate membranes and thin films.

4.1. *Physical dispersion of CDs in hybrid organic-inorganic sol-gel materials*

CDs-hybrids can be easily prepared through the silane's hydrolysis-polycondensation process in presence of CDs, under the catalysis of an acidic or alkaline medium.

There are many kinds of reports demonstrating the use of sol-gels as matrices for CDs. Some popular precursors are shown in Fig. 5, such as tetraethyl orthosilicate (TEOS) [85–87], 3-aminopropyl triethoxysilane

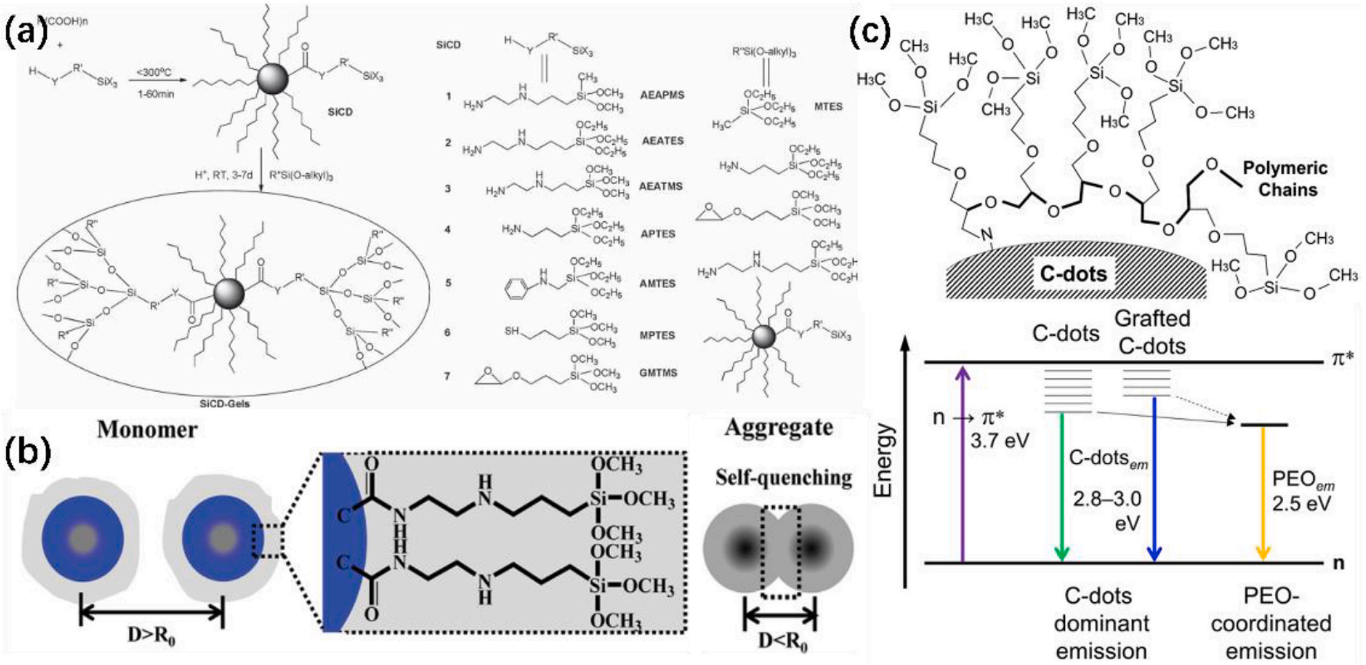

Fig. 6. Organosilane-functionalized CDs: (a) Seven types of silane functionalized CDs with citric acid as carbon precursor [97], (b) Self-quenching-resistant fluorescent silane functionalized CDs [98], (c) GPTMS-grafted CDs with PL shift [103]. (a) Reprinted with permission from Ref. [97]. Copyright 2012, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany. (b) Reprinted with permission from Ref. [98]. Copyright 2017, Royal Society of Chemistry. (c) Reprinted with permission from Ref. [103]. Copyright 2017, Springer Nature.

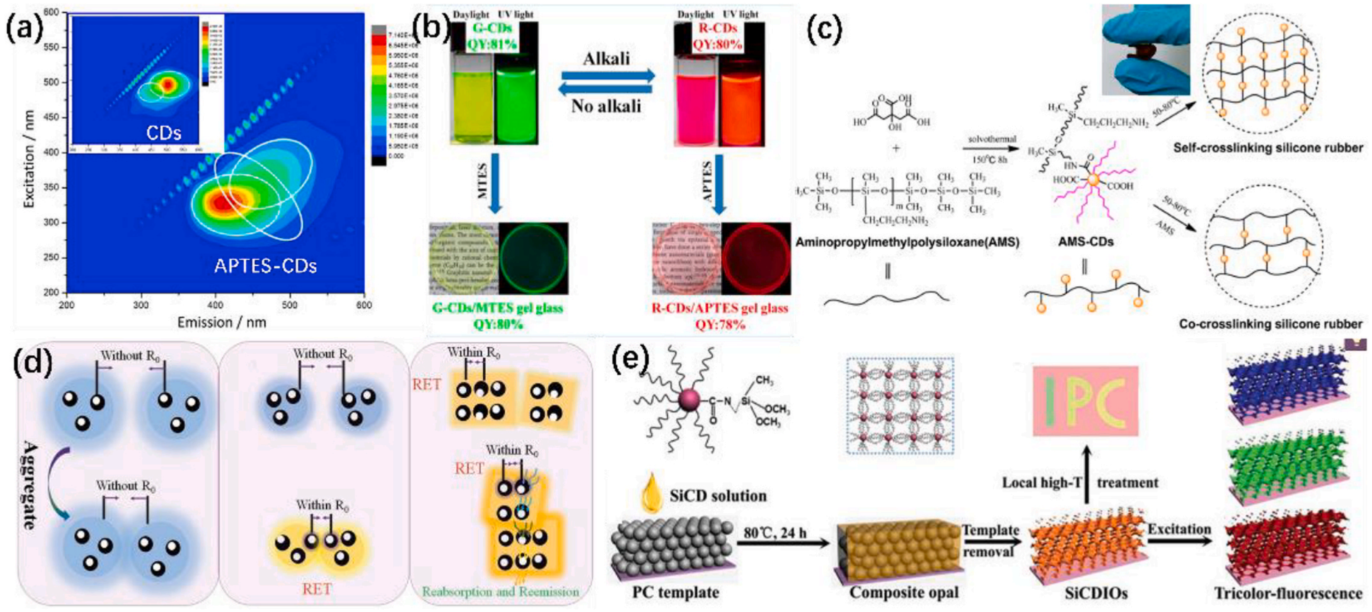

Fig. 7. Optical properties of CDs-hybrid composites: (a) The improvement of PL from CDs after APTES-functionalization [105], (b) CDs with reversibly switchable green−red emissions in MTES and APTES gels [106], (c) Flexible fluorescent silicone rubbers from the cross-linking of polysiloxane functionalized CDs [107], (d) Concentration-caused bathochromic shift of APTES-CDs [108], (e) Inverse opals based on organosilane-polymerized CDs [109]. (a) Reprinted with permission from Ref. [105]. Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany. (b) Reprinted with permission from Ref. [106]. Copyright 2018, American Chemical Society. (c) Reprinted with permission from Ref. [107]. Copyright 2016, American Chemical Society. (d) Reprinted with permission from Ref. [108]. Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany. (e) Reprinted with permission from Ref. [109]. Copyright 2018, Royal Society of Chemistry. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

(APTES) [88,89], MTES [90,91], alkoxides containing epoxy functional groups [92,93], and tetramethyl orthosilicate (TMOS) [94]. The hybrid nanocomposites exhibit good thermal and chemical stability, as well as excellent fluorescence.

A silica-polymer matrix has been also developed to support the CDs solid-state emission [95,96]. For example, Jiang et al. [95] have prepared CDs-SiO_2 by mixing the CDs produced from *m*-phenylenediamine with colloidal nanosilica; then, PVA solutions have been employed to prepare CDs-SiO_2-PVA films. The obtained composite films show both to be water and oxygen insensitive long afterglow at room temperature, which can be used to get moisture-related information.

4.2. *Organosilane-functionalized CDs*

To realize high-performance optical devices based on CDs at solid state, organosilane-functionalized CDs have been investigated. Organosilanes take part in the CDs preparation process as a functional agent [97–101]. As shown in Fig. 5a, Xie et al. [97] have prepared multi-types of organosilane-functionalized CDs using citric acid as carbon precursor and seven kinds of silanes as coupling agents through one-step hydrolysis. Silane-CDs also possess self-quenching-resistant fluorescence, because the organosilane-chains around CDs can weaken the effect of aggregation and decrease π-π interaction, which avoid ACQ effects (see Fig. 5b) [98].

Interestingly, the organosilane can directly work as both carbon precursor and functional agent. Shih et al. [102] have synthesized blue emitting silane-CDs by carbonizing APTES using hydrothermal route; the obtained blue dots could also emit in the green region after high-temperature calcination. The nanocomposites show good stability and electrocatalytic activity for the oxygen reduction reaction, which suggests a potential application as catalyst for fuel cells.

Silane functionalized CDs can also be prepared by using organosilanes to modify the as-prepared CDs [103,104]. Suzuki and co-workers [103] have grafted 3-glycidyloxypropyl trimethoxysilane (GPTMS) onto CDs via reaction between the epoxy in GPTMS and the amine groups of CDs using titanium chloride as catalyst. They have found that GPTMS-grafted CDs showed a new emission at 490 nm, overlapping with the original emission at 430 nm from pristine CDs. As shown in Fig. 6c the polyethylene oxide species from ring-opening of GPTMS produces a PL shift via hydrogen bonding interactions.

4.3. *Empowered properties from CD-hybrids*

The composition of a hybrid sol-gel material has a direct influence on the emissive performances of the CDs [105–110]. CDs synthesized by citric acid pyrolysis results weakly luminescent in aqueous solution. Ludmerczki et al. [105] have found that the CD surface modification by APTES reduces the quenching of fluorescence due to the formation of a silica stabilizing layer (see Fig. 7a).

Interestingly, the optical properties of CDs are highly dependent on the organosilicon compound and the resulting solution pH (neutral or alkaline). Yuan and co-workers [106] have reported a species of CDs with reversibly switching ability between green and red emission in no-alkaline or alkaline solutions. As shown in Fig. 7b, when the CDs are incorporated into MTES- (no-alkaline) and APTES-hybrid materials (alkaline), the system also shows green and red fluorescence, respectively. Simultaneously, the high QY of CDs is retained upon incorporation into the solid-state matrix. Apart from silane, Wang et al. [107] have developed polysiloxane functionalized CDs using aminopropyl methyl polysiloxane (AMS). The polysiloxane-CDs have formed 3D flexible fluorescent silicone rubbers by self-cross-linking or co-linking with AMS (Fig. 7c). The composite provides an original tool for flexible optoelectronic devices.

Besides the color change induced by the solvent, the CDs often exhibit shift bathochromic with a change of concentration, along with a QY loss. Zhan et al. [108] have prepared a series of CDs from citric acid and APTES via a solvothermal route. When they changed the citric acid - APTES molar ratio from 0.17 to 1.3, the CD emission showed a bathochromic shift from 452 to 564 nm. As shown in Fig. 7d, the distance of CDs decreases with the rise of citric acid content and the resonance

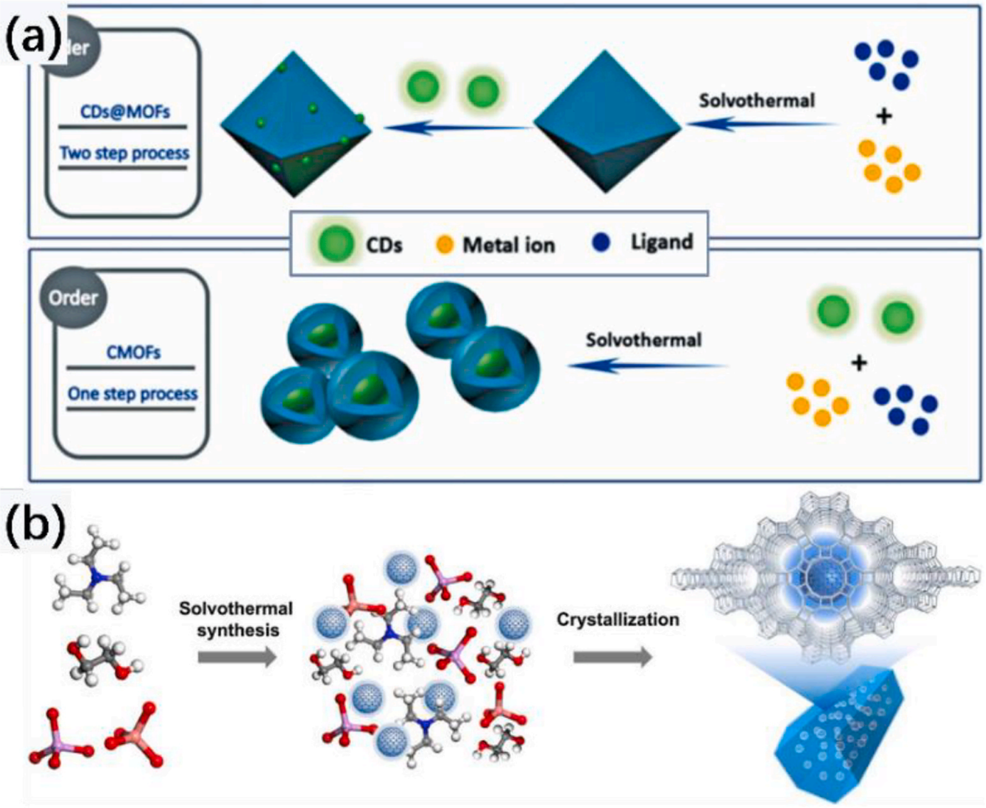

Fig. 8. CDs in porous materials: (a) CDs-MOFs composites [111], and (b) CDs-zeolite composites [114]. (a) Reprinted with permission from Ref. [111]. Copyright 2019, Elsevier Ltd. (b) Reprinted with permission from Ref. [114]. Copyright 2017, American Association for the Advancement of Science.

energy transfer causes the emission redshift.

Organosilane-polymerized CDs are suitable precursors for inverse opals [109,110]. For example, Liu and co-workers [109] have prepared micro-patterned inverse opals based on silane CDs, showing multi-color fluorescence (Fig. 7e).

5. Other materials as solid-state matrices

Beyond the polymers or hybrids as solid-state matrices, other options have been also considered. They include porous and, layered materials, inorganic salts, metal oxides, and even acid molecules. These hosts can also provide new interesting features to CDs.

5.1. Porous materials

Important examples of porous materials employed as hosts for CDs are metal-organic frameworks (MOFs) [111–113], and zeolites [114–116].

Ma et al. [111] have proposed two methods to combine CDs and MOFs (Fig. 8a). CDs-MOFs nanocomposites have been prepared by a conventional two-step strategy, mixing CDs and as-prepared MOFs. On the other hand, CDs-MOFs have also been obtained via a one-step approach, adding CDs into MOF raw precursors before reaction. Compared with the excitation-dependent PL of pristine CDs, CDs-MOFs exhibited a red-shift and excitation-independent fluorescence, which has been attributed to quantum confinement effect. On the contrary, one step synthesis CDs-MOFs showed a blue-shift and excitation-independent emission. These results confirm the importance of the hosting matrix on the CD properties and, in particular, the role of the synthesis route. Additionally, Gu and co-workers [112] have found that the size of CDs can be well controlled by using different MOFs as a template. He et al. [113] have synthesized CDs-MOFs with tunable size and fluorescence intensity as a function of CDs and precursor amount, paving the way to fluorescence imaging and pH-responsive drug delivery.

Fig. 8b shows an example of a CD-zeolite composite prepared by in-situ embedding of CDs into a zeolite matrix via solvothermal route, whose QYs and lifetime can reach up to 52% and 350 ms, respectively, at room temperature and in air [114]. The authors have hypothesized a decisive role of zeolitic host matrix to suppress the non-radiation and hinder oxygen-quenching. Accordingly, Wang et al. [115] have been able to adjust and improve the room temperature phosphorescence by implanting CDs into an Mn-framework, by the hydrothermal method.

5.2. Layered materials

Boron nitride nanosheets (BNNSs) possess a high thermal conductivity and can be applied as a thermal quenching-resistant platform. As shown in Fig. 9a, Cheng et al. [117] have prepared CDs/BNNSs hybrids through an electrostatic assembly method. The authors have investigated the photoluminescence of the hybrid as a function of temperature from 30 to 150 °C, revealing no significant efficiency loss. Moreover, the emission resulted dependent on the BNNS content, which promotes an enhancement of the yellow-red component. Although further investigation on the interaction between CDs and layered material is mandatory, this kind of composite can be a good candidate for the development of thermal quenching-resistant phosphors.

Layered double hydroxides (LDHs) are inorganic systems, where the metal cations (M) occupy octahedral positions of the hydroxide layers in a high ordered arrangement according to the formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}$ $(A^{n-})_{x/n}\cdot mH_2O$ [118]. As specified by Bai and co-workers [118], CD optical properties may benefit from a CDs/LDH heterostructure, thanks to the rigid and confined orderly layers (Fig. 9b). Herein, CDs/LDH have been obtained by directly carbonizing the ethylene diamine tetraacetic acid (EDTA) existing in LDHs, and EDTA-LDHs have been prepared by adding EDTA in the process of LDH

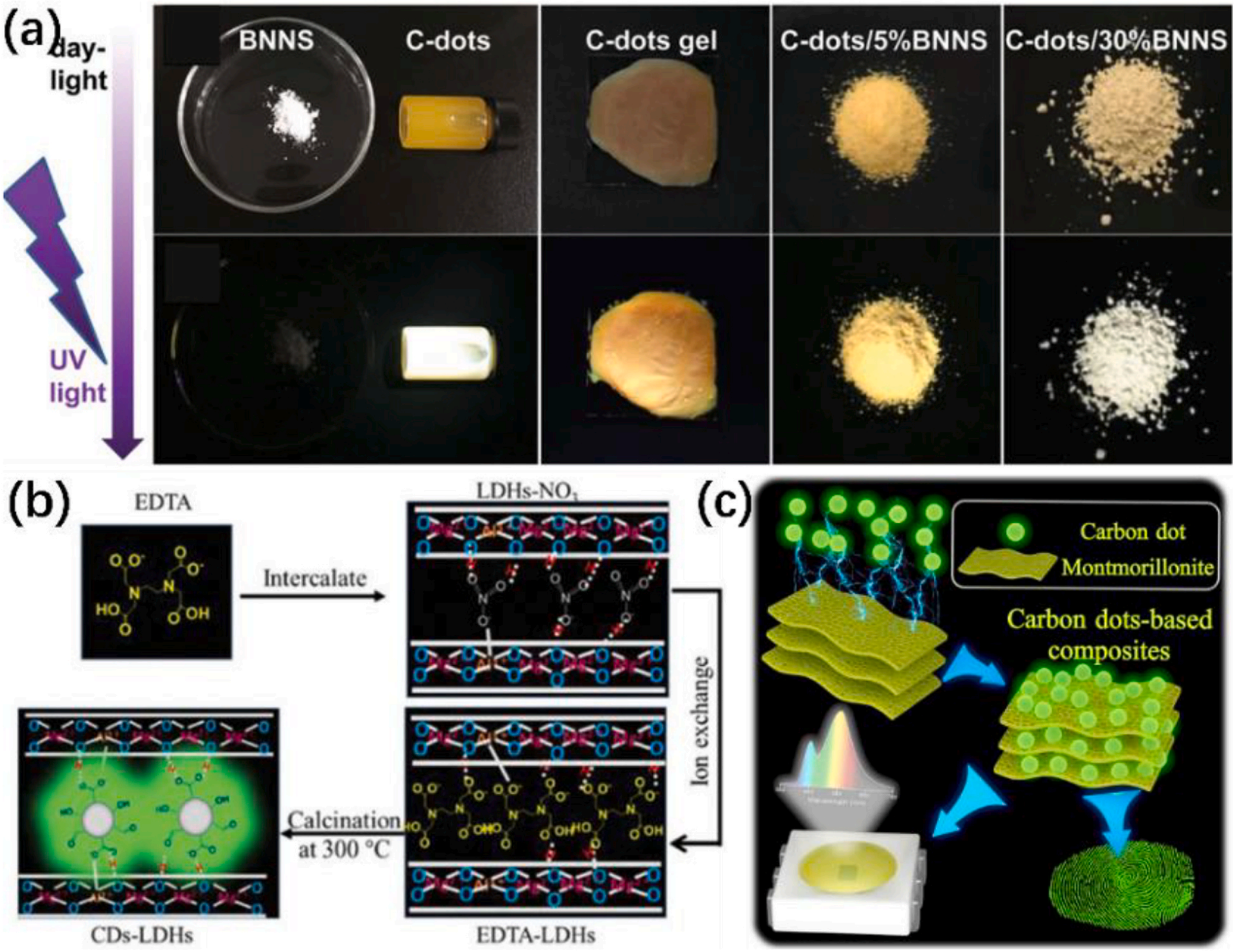

Fig. 9. CDs in layered materials: (a) CDs/BNNSs hybrids [117], (b) CDs-LDHs composites [118], and (c) CDs-montmorillonite composites [119]. (a) Reprinted with permission from Ref. [117]. Copyright 2019, Royal Society of Chemistry. (b) Reprinted with permission from Ref. [118]. Copyright 2017, Royal Society of Chemistry. (c) Reprinted with permission from Refs. [119]. Copyright 2019, Elsevier Inc.

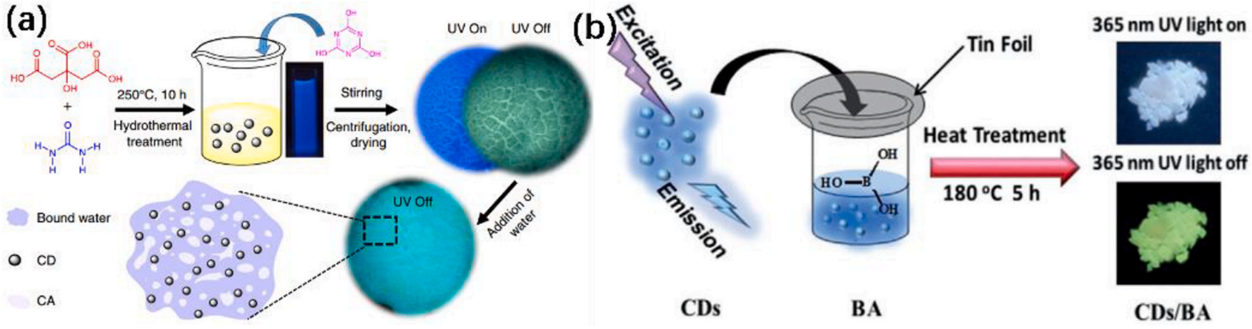

Fig. 10. CDs in acid molecules: (a) CDs-cyanuric acid [120], and (b) CDs-boric acid [121]. (a) Reprinted with permission from Ref. [120]. Copyright 2018, Springer Nature. (b) Reprinted with permission from Ref. [121]. Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

synthesis. Furthermore, the suitable choice of non-noble metal and the intrinsic stability of the inorganic matrix, can suppress non-radiative channels and improve singlet and triplet radiative recombination.

Another material that has been taking into account for the preparation of CD-nanocomposites is montmorillonite (MMT), whose crystal structure consists of overlapped pyrophyllite layers along c-axis. With its low-cost and low-toxicity, MMT has potential applications as host for optical active materials (Fig. 9c) [119]. Citric acid and urea derived CDs can be easily embedded into a MMT matrix by freeze-drying CDs and MMT mixed aqueous liquid after stirring, which shows strong green emission. This hybrid has been successfully applied to obtain dichromatic white LEDs. Additionally, CDs-MMT have been tested as labeling markers for applications in the areas of healthcare and forensic science.

5.3. Acid molecules

Recently, some acid molecules have been tested as matrices for CDs and metal-free phosphorescence at room temperature. Li et al. [120] have used water molecules to build stable hydrogen-bonded networks between CDs and cyanuric acid (CA) (Fig. 10a). In the proposed method,

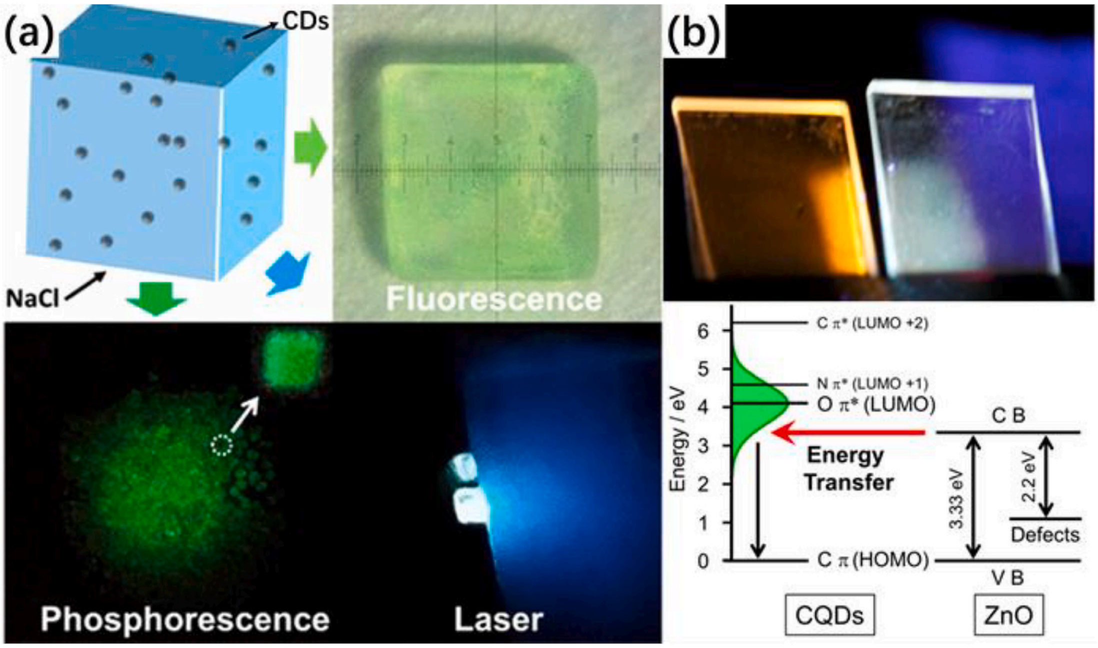

Fig. 11. CDs in acid molecules inorganic salts or metal oxides: (a) CDs-NaCl hybrid crystals [122], and (b) CDs-ZnO films [125]. (a) Reprinted with permission from Ref. [122]. Copyright 2017, American Chemical Society. (b) Reprinted with permission from Ref. [125]. Copyright 2015, American Chemical Society.

a mixture of cyanuric acid and CDs was treated in hydrothermal conditions at 250 °C for 10 h. The addition of water to the CA-CDs powder induced an increase of phosphorescence intensity of about three times, while the phosphorescence lifetime reached up to 687 ms. The authors have proposed the existence of a CA - CD interaction through highly ordered water molecules, which prevents the phosphorescence quenching, as the most probable mechanism.

Li and co-workers [121] have used boric acid as solid matrix for CDs, showing multicolor room temperature afterglow, with a phosphorescence lifetime up to 1.6 s (Fig. 10b). According to the authors, the boron atoms and the consequent formation of boron-carbon bonds reduce the energy gap between singlet and triplet states, promoting a more efficient intersystem crossing and enhancing room temperature phosphorescence.

5.4. Inorganic salts or metal oxides

The crystallization of inorganic salts, such as NaCl, KCl, and KBr, leads to the formation of transparent matrices, which can be processed into solid-state luminescent crystals by embedding CDs. The inorganic salt crystals possess good UV and thermal stability, with high transparency both in the UV and visible ranges. Thus, salt crystals serving as host matrices preserve the CD optical properties and protect them from extreme environment. As shown in Fig. 11a, a liquid-liquid diffusion-assisted crystallization process has been used to incorporate the CDs into a NaCl matrix [122]. The CDs-NaCl hybrid crystals show phosphorescence with a lifetime of 314 ms, and can be used as a whispering gallery mode resonant cavity for lasing emission.

Kim and co-workers [123] have compared the properties of inorganic salt crystals (NaCl, KCl, KBr) and silica as a matrix for CDs. Among the others, NaCl demonstrates the most suitable characteristics to preserve CDs fluorescence stability under UV irradiation. After 250 h of UV exposure, CDs-NaCl composites lose 30% of initial efficiency. In general, it has been found that the PL stability of CDs-crystals extends by 15 times under UV radiation and 6 times under heat process in comparison with CDs-silica. Zhou et al. [124] have fabricated CDs-$BaSO_4$ hybrids through an electrostatic assembly route. The emission of obtained hybrid-phosphors shows not only excellent thermal properties and photostability but also remarkable resistance to strong acid/alkali and common organic solvents.

Porous metal oxides have also been tested for developing fluorescent CDs. Fig. 11b shows an example of CDs-ZnO nanocomposites [125]. The PL properties of ZnO derived from the presence of defects are modulated by the mutual interaction with CDs, which, in turn, present aggregation dependent optical properties. The number of CDs in the ZnO matrix can effectively tune the emission of the optically active matrix in the visible range. A small percentage of CDs quenches the orange emission due to interstitial oxygen defects. At increasing CD concentrations, an enhancement of green emission has been observed. The ZnO matrix can be re-used for another impregnation cycle after CDs are removed by thermal annealing [126]. He et al. [127] have designed an oxygen-sensor based on fluorescence by embedding blue, green and red emissive CDs into mesoporous Al_2O_3. The composites have a high fluorescent sensitivity with a linear oxygen volume range from 0 to 100, and a fast response/regeneration of 2–4 s.

6. Summary and future outlook

The design of CD solid-state nanocomposites requires tailored solutions, which focus on the optimization of the structure-properties relationship. Uniform distribution of CDs in the matrix is necessary to avoid quenching effects and modulating at the same time the optical response. In the solid-state, the CD photoluminescent properties are affected by oxidation and aggregation that contribute to lower the quantum efficiency and to change the absorption and fluorescence properties. The realization of CDs with self-quenching-resistant properties is the most direct strategy to achieve efficient solid-state emitting CD systems. When deprived of the solvent, the carbon nanoparticles suffer the effect of a strong surface interaction accompanied by quenching and spectral change. The reduction of sp^2 domains has proven to be an advantageous method to counteract the loss of emission efficiency. However, the obtained CDs are usually in a powder state and need further processes and manipulation to be employed in practical applications.

Despite the remarkable progress in creating self-quenching resistant CDs, the way to incorporate them into matrices is still the most successful one. In addition, one can take advantage of using a CDs/matrix heterostructure to improve the properties of CDs or even extending their field of application.

The popular matrices include polymers and hybrid organic-inorganic sol-gel materials. In general, organic polymers represent the most common option as a host material for CDs. The deriving polymeric matrices can inherit the monomer characteristics, e.g. polarity, which allows the conservation of optical properties from solutions to solid composites. Moreover, the flexibility and plasticity of polymeric structures permit the fabrication of matrices with various forms and shapes. The necessity to dissolve the polymer to incorporate the CDs may, however, represents a limitation if it requires the use of a specific organic solvent.

Sol-gel processing is another flexible tool for the preparation of a host matrix. Hybrid materials represent an alternative to organic polymers with improved performances and durability. Hybrids, in general, exhibit better chemical durability and thermal stability than polymers at high temperature and under UV irradiation. Besides, mesoporous and layered materials are proved to be an excellent choice as support for fluorescent CDs in solid-state.

A common problem that can be observed both for polymeric and hybrid organic-inorganic sol-gel materials is the limited physical dispersion of CDs into the matrices. Therefore, the CDs must be properly functionalized to promote the copolymerization between CDs and matrices. This can include the use of polymers and organosilanes. The general choice is vinyl-functionalization for polymers via addition polymerization reaction. Several types of organosilanes can be grafted on CDs and the grafting process can also be directly obtained when the polymer or organosilane takes part in the CDs preparation process. Nevertheless, this type of CDs is sometimes unable to meet the requirement for high-quality applications due to difficulties often encountered during purification.

Many other alternatives to solid-state CDs nanocomposites are reported in the scientific literature. Among the others, the use of acid molecules, inorganic salt crystals, and metal oxides represent viable strategies, but the choice is largely dependent on the requirements and the final performance of the device. In general, coupling the design of the CDs in terms of surface and composition with that of the host matrix is mandatory for achieving a precise design of the optical performances. Hosting CDs in special matrices can be convenient both to preserve the optical properties of the CDs and to give the host material new and interesting properties. Hybrid systems, in fact, allow realizing at low cost, efficient bulk or freestanding films, which can, at the same time, improve the material flexibility or mechanical strength. Moreover, thanks to the mutual interaction, it is possible promoting a strong redshift of CD emission and cover new spectral regions. This effect has already been demonstrated for CDs emitting in the red. Still, it remains unanswered whether this approach can also be used to reach infrared emission. Another very common effect in CDs/matrix hybrids is the inhibition of phosphorescence quenching or the extension of luminescence lifetime, which is not observable in CDs alone. In addition, new effects have been measured for targeted applications, including temperature-dependent emission. Thanks to high thermal conductivity matrices, the efficiency and photostability of CDs is preserved as a function of temperature. The incorporation in porous materials and the high surface area available, opens the door to new high-sensitivity sensors that exploit the efficient fluorescence properties of CDs.

So far, CDs have demonstrated a high potential for solid-state applications as shown by the different examples given in this article. However, optical and photonic devices are still far from being realized. Many factors contribute to a slowdown in CD applications. Among these, the actual structure of CDs and the origin of fluorescence is far from being fully understood for a wide variety of CDs. Moreover, for many of them, the origin of the optical properties is to be found in molecular fluorophores and particular functional groups, which strongly interact with the chemical environment, limiting the QY and significantly modifying the spectral characteristics.

Moving towards solid-state does not allow trivial solutions, but a high control of the structural and chemical characteristics of CDs are prerequisites. Precise control of the CDs surfaces, the study of possible solvatochromic effects and the interaction of matrix precursors are of the fundamental importance for the development of CDs-based devices able to compete with more established systems, such as quantum dots and semiconductor nanostructures.

In the future, it will be crucial exploring in-depth the interaction mechanisms of CDs and matrix. The comprehension of the relationships between CDs properties and matrices would contribute to choosing the proper solid-state host for tailored applications.

Acknowledgments

This work was supported by Fondi di Ateneo 2019 of the University of Sassari. L.S. gratefully acknowledges for the financial support Programma Operativo Nazionale (PON) Ricerca e Innovazione 2014-2020-Linea 1. Italian Ministry of Education, University and Research (MIUR) is acknowledged for funding through the project PRIN 2017 NO. 2017W75RAE.

Abbreviations

CD	Carbon dot
PL	Photoluminescence
QY	Quantum yield
ACQ	Aggregation-caused quenching
PVA	Polyvinyl alcohol
PVP	Polyvinylpyrrolidone
PMMA	Poly(methyl methacrylate)
PDMS	Polydimethylsiloxane
PVB	Polyvinyl butyral
PEG	Polyethylene glycol
PU	Polyurethane
PEI	Polyethyleneimine
PS	Polystyrene
MTES	Methyltriethoxysilane
TEOS	Tetraethyl orthosilicate
APTES	3-Aminopropyl triethoxysilane
TMOS	Tetramethyl orthosilicate
GPTMS	3-Glycidyloxypropyl trimethoxysilane
MOF	Metal-organic framework
BNNS	Boron nitride nanosheet
LDH	Layered double hydroxide
EDTA	Ethylene diamine tetraacetic acid
MMT	Montmorillonite
CA	Cyanuric acid

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