

Metal Ions Doped-Carbon Dots: Synthetic Approaches, Physicochemical Properties and Their Applications

Dang Dinh Khoi^{1*}, Pham Thanh Tung^{1,2}

¹Faculty of Chemical and Food Technology, Ho Chi Minh City University of Technology and Education, Viet Nam

²Institute of Food Science and Technology, Hungarian University of Agriculture and Life Sciences, Hungary

* Corresponding author. Email: khoidd@hcmute.edu.vn

ARTICLE INFO

Received: 15/03/2022
Revised: 21/05/2022
Accepted: 21/09/2022
Published: 28/12/2022

KEYWORDS

metal ions doped-carbon dots (M-CDs);
chemical sensing;
biomedical imaging;
phototherapy;
optoelectronics.

ABSTRACT

Carbon dots (CDs) are the most promising members of the carbon family with superior properties such as ultrasmall size, high solubility, low cytotoxicity, and inherent fluorescence endows their potential for diverse applications. There are several discovered methods to improve their properties and the extent of their applications. Possible approaches are doping or surface passivation of CDs to enhance their properties, visible light absorption, and quantum yields by controlling their size, morphology, structure, and band gap energy. As an efficient method to improve the intrinsic properties of carbon dots, doping CDs with heteroatoms such as nonmetallic and metallic atoms has received increasing attention from researchers around the globe. Recently, metal ions doped-carbon dots (M-CDs) have emerged as an important one of nanomaterials with numerous applications. In this paper, we will summarize the state-of-the-art knowledge of M-CDs. The synthetic methods for M-CDs, the novel physicochemical properties originating from the doping of metal ions, and their applications in chemical sensing, biological imaging, phototherapy, optoelectronics, and catalysis will also be highlighted. Furthermore, we will describe challenges in preparing M-CDs and an outlook for their future development.

Doi: <https://doi.org/10.54644/jte.73.2022.1167>

Copyright © JTE. This is an open access article distributed under the terms and conditions of the [Creative Commons Attribution-NonCommercial 4.0 International License](https://creativecommons.org/licenses/by-nc/4.0/) which permits unrestricted use, distribution, and reproduction in any medium for non-commercial purpose, provided the original work is properly cited.

1. Introduction

Photoluminescent carbon dots (CDs), which usually can be classified into carbon nanodots, carbon quantum dots, and graphene quantum dots, have aroused much attention since they were accidentally discovered during the electrophoretic fractionation of carbon nanotubes in 2004 [1]. Compared to other photoluminescent materials as organic dyes or traditional semiconductor quantum dots (QDs), novel CDs have the advantages of easy preparation and surface modification, good photostability, water dispersibility, as well as tunable fluorescence properties, excellent biocompatibility, and low cytotoxicity [2] – [3]. Typically, the core of CDs consists of crystalline sp^2 carbon, while the surface is composed of functional groups such as carboxyl, amino, and hydroxyl [2] – [4]. This unique nanostructure endows CDs with special physicochemical properties, enabling their extensive applications in chemical sensing, biological imaging, phototherapy, optoelectronic devices, and so on [5] – [11].

Chemical heteroatoms doping, which is convenient for large-scale synthesis, aims to change chemical composition, electronic structures, and nanostructure by introducing non-metal atomic impurities and metal ions into CDs that endow them with various intrinsic properties. Previous reports show that most non-metallic heteroatoms doped-CDs can obtain via facile synthetic methods from raw materials that have enhancement of quantum yields (QYs) of CDs, and the extension of their applications due to the non-metallic heteroatoms doping [12] – [15]. Compared to non-metallic atoms, metal ions have larger atomic radii, more electrons, and unoccupied orbitals. Therefore, after doping CDs with metal ions, their electron density distribution and energy gap undergo drastic changes, enabling the adjustment of the CDs' physical and chemical properties [16] – [17].

Although there are various review articles on the preparation and applications of heteroatom-doped CDs, merely a few reviews focused on M-CDs [18] – [20]. However, research on M-CDs has developed rapidly, and many synthesis approaches and applications have been reported recently. Therefore, there is a desire to summarise these advanced materials and state-of-the-art techniques for designing them. Furthermore, the relationship between the unique properties of M-CDs and metal ions-doping needs to be analyzed in-depth.

In this paper, various synthetic routes adopted to prepare M-CDs, their specific physicochemical properties derived from the different kinds of dopants, and applications of M-CDs will be covered and discussed. More importantly, based on the available work on M-CDs, potential challenges and obstacles encountered in the development of M-CDs will be comprehensively summarized and perspectives for the further exploration of novel applications will be proposed in this review.

2. Synthetic approaches

The convenient synthetic routes for M-CDs focus on the chemical reaction between the relative metallic compound and organic molecules under certain reaction conditions, which can be divided into two main categories: one-step route and multi-step route. The one-step synthesis methods include the hydrothermal method, solvothermal method, microwave method, pyrolysis method, and ultrasonic chemical method. Besides, M-CDs can also be prepared through multi-step routes by exfoliating the large metal ions doped carbonaceous materials, which are obtained through extra metal ions doping step into the cleavage.

2.1. One-step synthetic routes

2.1.1. Solvothermal/hydrothermal method

The solvothermal method is the most widely adopted route for preparation of M-CDs due to its low cost, high efficiency, and convenient implementation. This method usually refers to treating the mixture of carbon sources and metallic salts with solvents at high temperatures for several hours. Up to date, CDs doped with manganese (Mn) [21], magnesium (Mg) [22], zinc (Zn) [23], gadolinium (Gd) [24], cobalt (Co) [25], and silver (Ag) [26] have been prepared with this method. For example, a solvothermal method for the preparation of Co-CDs has been carried out by Zhang et al [25]. In their work, Co-CDs were synthesized by using 1-(2-Pyridylazo)-2-naphthol (PAN) and CoCl₂ in the presence of ethanol via a solvothermal process. The Co-CDs product was then applied for the detection of Cr⁴⁺ ions by quenching effect (Fig. 1) [25].

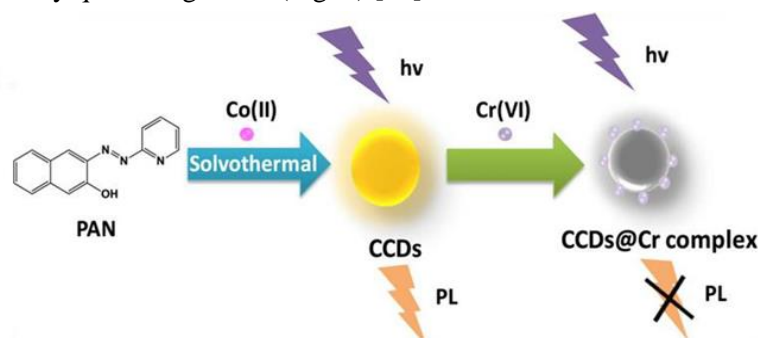


Fig. 1. Schematic illustration of the solvothermal synthesis of Co-CDs.

However, the solvothermal method has the disadvantage of employing organic solvents, which are toxic, expensive, and may cause serious damage to human health. In contrast, water is green and cheap solvent; thus, the hydrothermal method for preparing M-CDs has become favored by researchers. In 2019, Cr-CDs were prepared via the hydrothermal treatment of Tris(2,4-pentanedionato)chromium(III) and polyethyleneimine (PEI) at 200°C for 12 h by Jiang and colleagues [27]. Cr-CDs in an aqueous solution exhibited blue-green color emission with a QY of 20% and were used as a fluorescence probe for p-nitrophenol (p-NP) [27]. To date, single-doped M-CDs such as copper-doped CDs (Cu-CDs) [28], and two kinds of heteroatoms co-doped CDs like magnesium and nitrogen co-doped CDs (Mg, N-CDs) [29] have been prepared with this method.

2.1.2. Microwave method

The microwave method is an efficient route, which can be finished in a relatively short time, around several minutes. As an example, Yang's group has reported a simple process for preparing Fe, N-CDs via the microwave method. In a typical procedure, L-tartaric acid, urea, and FeCl₃·6H₂O were dissolved in oleic acid as the reaction solvent. The solution was heated to 200°C for 10 min, then cooled down to room temperature. After removing the unreacted oleic acid and purifying via silica column chromatography using a mixture of ethyl acetate and ethanol as the eluent, the product Fe, N-CDs were finally re-dispersed into water (Fig. 2) [30]. The TEM image showed that the Fe, N-CDs were distributed uniformly. Also, the lattice fringes of 0.22 nm on their surface indicated the [100] facet of sp² graphitic carbon. In addition, the Gd-CDs, and Eu-CDs also have been obtained with the microwave method [31] – [32].

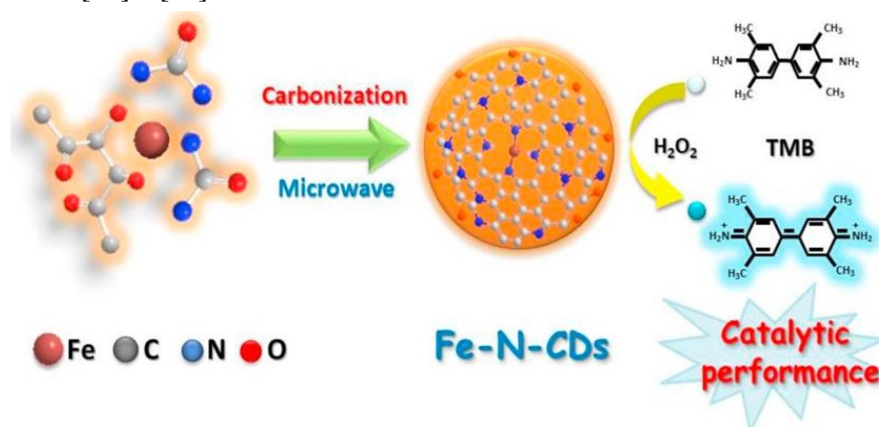


Fig. 2. Schematic illustration of the microwave synthesis of Fe, N-CDs.

2.1.3. Pyrolysis

Pyrolysis is a facile method commonly used for preparing M-CDs [20]. For example, using Na₂[Cu(EDTA)] as a precursor, Wu et al prepared Cu-CDs via the pyrolysis route (Fig. 3) [33]. After heating the precursor at a high temperature for two hours, the product was dissolved in water. The obtained solution was ultrasonicated, centrifuged, filtered, and then dialyzed to produce Cu-CDs. In addition to Cu-CDs, many other M-CQDs also have been prepared via the pyrolysis route, such as Ce-CDs [34], Tb-CDs [35], Ru-CDs [36], dual-metal doped CDs (Fe, Cu-CDs) [37], and so forth. However, the M-CDs prepared with the pyrolysis process have disadvantages due to their relatively large sizes as being poorly hydrophilic, difficult for further functionalization, and easy to accumulate. Previous publications shown that larger materials could be easily broken down into smaller parts with acidic oxidation; thus, treating the large products from pyrolysis with acidic oxidation could effectively overcome the limitations of pyrolysis [18].

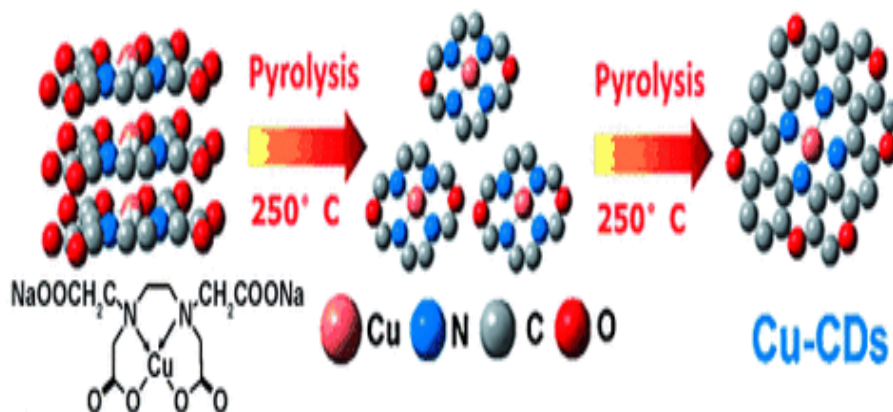


Fig. 3. Schematic illustration of the pyrolysis synthesis of Fe, N-CDs.

2.1.4. Ultrasonic method

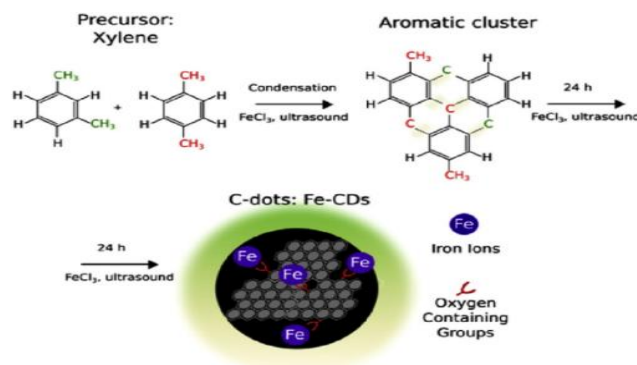


Fig. 4. Schematic illustration of the ultrasonic synthesis of Fe, N-CDs.

Ultrasound irradiation, which generates heat, has also been used to prepare M-CDs. It should be noted that the ultrasound-assisted method is generally time-consuming. On the contrary, the microwave-assisted method is time-saving and takes only a few minutes because microwave radiation generates high heat rapidly to dehydrate and carbonize the carbon sources. For example, Bourlinos et al used xylene, ethylbenzene, and FeCl₃ as precursors to prepare Fe-CDs in a sonication bath for 24 h, resulting in a deep brown suspension as shown in Fig. 4 [38]. This approach also has been used to prepare numerous types of M-CDs, such as Gd-CDs [39], Au-CDs [40], Eu-CDs [41], Fe-CDs [42], and Zn-CDs [43].

2.2. Multi-step synthetic routes

In some cases, multi-step synthesis routes are employed for the effective doping of metal ions into CDs. For example, Chen et al found that when direct pyrolysis of Gd-diethylene triamine pentaacetic acid (Gd-DTPA) in the air, the Gd-CDs were obtained with a broad size distribution [44]. To control the Gd-CDs size for the bio application, they first prepared mesoporous silica nanoparticles of different pore sizes via the cetyltrimethylammonium bromide-templated co-condensation method, which were used as reactors to load Gd precursors. Gd-CDs were fabricated with the desired size via the calcination process due to the limitation of the size of the silica cavity. In addition, Lin et al synthesized the Eu-CDs by firstly preparing Eu-doped graphene oxide via the hydrothermal method, then the obtained Eu-doped graphene oxide was treated with mixed strong concentrated acids of H₂SO₄ and HNO₃ to obtain Eu-CDs [45]. There were also other types of M-CDs prepared via this multi-step such as Fe-CDs [46] and Tb-CDs [47].

3. Physicochemical properties

Previous publications have shown that adding metal ions to CDs could change their pristine electronic structure of them, thus affecting the optical properties of M-CDs. In addition, not only the changing of optical properties occurred but also new physicochemical properties of M-CDs such as cytotoxicity have been detected so far.

3.1. Optical properties

Previous studies revealed that common CDs possess unique optical properties such as absorption, fluorescence (FL), chemiluminescence (CL), electrochemiluminescence (ECL), and up conversion luminescence. However, the study of M-CDs is still in a preliminary phase, that is only focused on the absorption and fluorescence properties of M-CDs. Although M-CDs differ from each other in the dopants and the detailed structures, M-CDs still share some similar optical properties. Most of the M-CDs have a strong and broad absorption band located between 200 nm and 600 nm (Fig. 5) [13]. While some of them possess a characteristic peak at nearly 225 nm [45,48], which is related to the π - π^* transition of the sp² domains, others show no obvious peak [49]. Because the existence of metallic dopants derives from the metal ions-to-graphite charge-transfer absorption, the absorbance of M-CDs is much higher than that of CDs in the visible region at the same concentration.

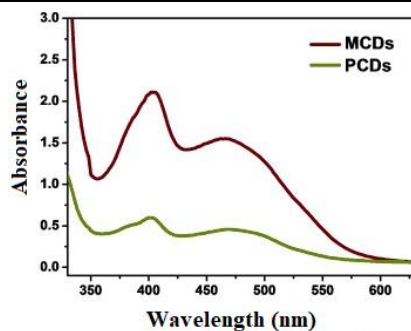


Fig. 5. Absorption spectra of pure CDs (PCDs) and Mn-CDs (MCDs).

Moreover, the obtained M-CDs can exhibit different color emission under 365 nm UV light including ultraviolet [46], blue [35] – [48], blue-green [51], green [31], yellow [13] and so on. The fluorescence emission peak of M-CDs is usually red-shift [13,45] and most M-CDs show excitation-dependent FL behavior compared with CDs [29]. As the excitation wavelength red-shifts, the emission peaks of M-CDs continuously shift to longer wavelengths with the intensity decreasing [52].

In addition, with various types and levels of metallic dopants, the QYs of M-CDs will be changed. Besides, the lifetime of M-CDs illustrated that the photoluminescence of M-CDs may induce by the radiative recombination of the carbon particle surface-trapped electrons and holes [50]. Therefore, doping metal ions on the surface-trapped electrons and structural properties of CDs, which disordered the carbon rings, improved electrons, and holes purging resulting from the newly produced emission energy traps will enhance the QYs of M-CDs [23,31].

3.2. Cytotoxicity

Because of the metal ions doping, the QYs of M-CDs will be enhanced obviously and considerably making M-CDs more feasible in bioimaging. However, the doping of metal ions also causes the problem of biotoxicity that should be noticed carefully when M-CDs are applied in bio-related fields. In the cytotoxicity study, cell counting kit-8 tests were conducted on human HeLa cells to evaluate the cytotoxicity of Gd-CDs and the results revealed that cell viability was comparable at a Gd-CDs concentration lower than $80 \text{ mg}\cdot\text{mL}^{-1}$ meaning M-CDs had low toxicity (Fig. 6) [53]. Moreover, Xu et al reported that no tissue pathological damage was derived from the intravenous injection of Gd-CDs solution by tail vein into the mice [54].

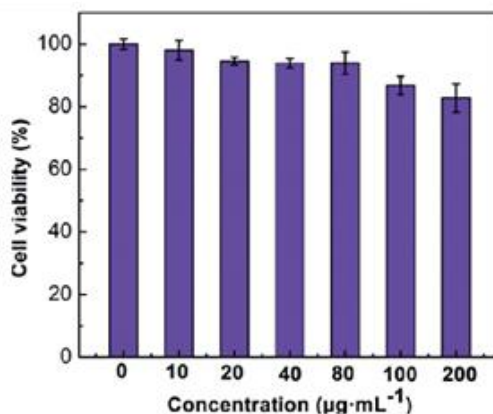


Fig. 6. Viability of HeLa cells incubated with various concentrations of Gd-CDs for 24 h.

4. Applications

4.1. Optical sensors

Optical sensors based on M-CDs have been applied because of their excellent photostability and rich binding sites [55]. The sensing mechanisms are mainly attributed to photo-induced electron transfer (PET), fluorescence resonance energy transfer (FRET), charge transfer, and the inner filter

effect (IFE) [56]. For example, Liu and co-workers synthesized germanium-doped CDs (Ge-CDs) using CA and Ge-132 as precursors via the pyrolysis method obtained Ge-CDs, which exhibited blue fluorescence with a QYs of 8.9%. The high QYs of the as-prepared Ge-CDs applied in sensing Hg^{2+} due to the strong coordination interactions of Hg^{2+} with $-OH$ and $-COOH$ groups on the surface of the Ge-CDs, thus quenching their FL [50]. In addition, M-CDs were also used for biomolecule detection. In a typical process, Hu et al prepared blue color emission Gd-CDs via the hydrothermal route using tryptophan, $GdCl_3$, and glucose. Because of the strong $\pi-\pi$ stacking interaction between the CMPs@GOx and the Gd-CDs, the FL of the Gd-CDs was quenched by the carbon complex of microparticle glucose oxidase (CMP-GOx) under the mechanism of FRET (Fig. 7) [57].

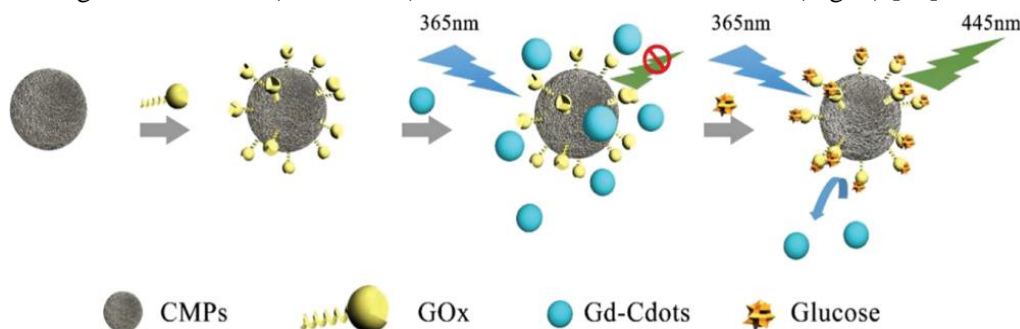


Fig. 7. The detection mechanism based on FRET between the Gd-Cdots and CMPs@GOx for glucose.

4.2. Bioimaging

CDs have been considered promising candidates in the field of fluorescent imaging (FLI), photoacoustic imaging (PAI) and magnetic resonance imaging (MRI) because of their outstanding FL stability, low toxicity, the absence of fluorescence blinking, adjustable excitation wavelength, good biocompatibility, as well as tunable emission wavelength [13]. Moreover, M-CDs have been employed as imaging and labeling agents for tracking molecular targets in living cells, tissues, and other biological systems [22] – [58]. For example, Sahu et al prepared orange fluorescent Mn-CDs with excellent cell penetration ability and low toxicity. The research results proved that the Mn-CDs is an ideal bioimaging reagent and have excellent biocompatibility, giving opportunities for intracellular and cell FLI [59]. In another process, Du et al prepared gadolinium-doped carbon dots (Gd-CDs) by a facile one-pot hydrothermal route designed for (MRI). The applications of Gd-CDs in bioimaging demonstrated that they have a relatively long circulation time (around 6h), and achieve efficient passive tumor targeting as they accumulate in the kidneys and can clear the bladder from the body. These experimental results have verified that Gd-CDs are favorable biocompatibility and possess great promise for MRI-guided radiotherapy of tumors (Fig. 8) [60].

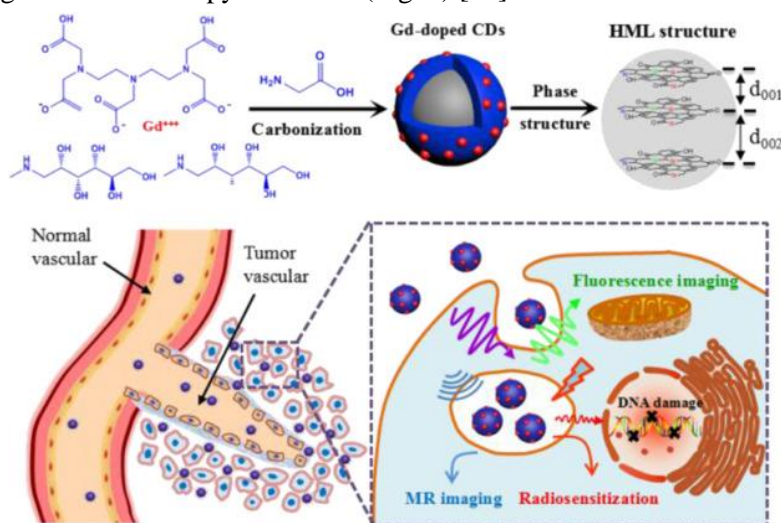


Fig. 8. Schematic illustrating the Synthesis of Gd-CDs and application in imaging.

4.3. Phototherapy

Phototherapy is a non-invasive cancer treatment in which phototherapy agents are used to convert light energy into reactive oxygen species (OH, $^1\text{O}_2$) or heat, leading to the local death of cancer cells. Phototherapy can be divided into photodynamic therapy (PDT) and photothermal therapy (PTT) [61]. Because of their unique optical properties, high water solubility, and photostability, M-CDs have been used as phototherapy agents [62]. For example, Guo and co-workers prepared Cu, N-CDs as a new class of NIR light-triggered therapeutic agents via a facile hydrothermal treatment of EDTA.2Na and CuCl_2 . It is believed that the N-Cu-N bonds enhanced the absorbance of the prepared Cu, N-CDs in the NIR region and promoted electron transfer during the photooxidation. Therefore, the Cu, N-CDs could generate $^1\text{O}_2$ and heat under NIR laser irradiation, thus acting as FLI and thermal imaging agents to enable the in vitro and in vivo PDT treatment processes (Fig. 9) [63].

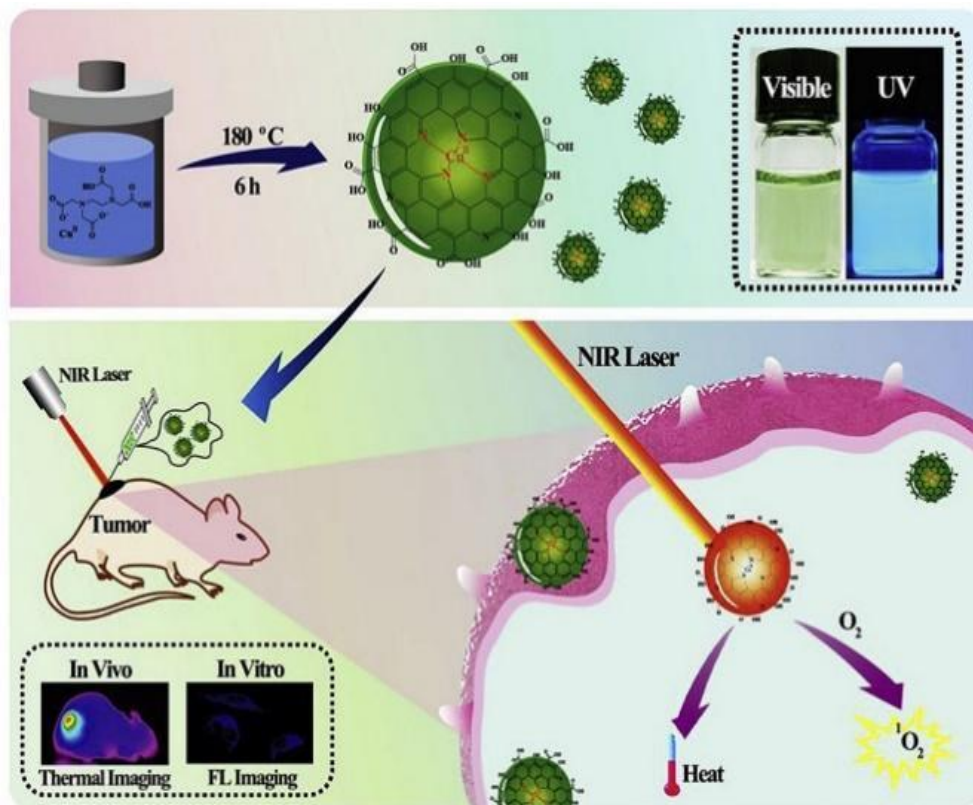


Fig. 9. Schematic illustrating the synthesis and the applications of Cu, N-CDs.

4.4. Optoelectronic devices

Light-emitting diode (LED) is an ideal light source because of its high efficiency, long lifetime, and low power consumption [64]. QDs have been considered a potential replacement for LEDs; however, their complex synthesis process and precursors are mostly toxic heavy metal ions that have restricted their practical application [65]. Interestingly, CDs possess fluorescence tunability, high photostability, low toxicity, environmental friendliness, and high electron mobility. These excellent properties make them a more suitable candidate for LED. Recently, researchers have focused on M-CDs with enhanced carrier recombination in the trap states on the surface of the novel M-CDs to improve the LED performance, ensure high QYs, and the ability to emit solid-state light in contrast to pure CDs. For instance, Cheng and co-workers prepared yellow color emission Zn-CDs with a high QYs of 51.2% using ZnCl_2 and CA as precursors. Due to the rapid radiative recombination of the electrons and holes trapped on the Zn-CDs, the Zn-CDs exhibited high QYs. The obtained Zn-CDs were successfully embedded into a white light-emitting diode (WLED). Furthermore, the Zn-CDs solution was used to create fluorescent patterns using inkjet printing resulting yellow fluorescence patterns as expected (Fig. 10) [66].

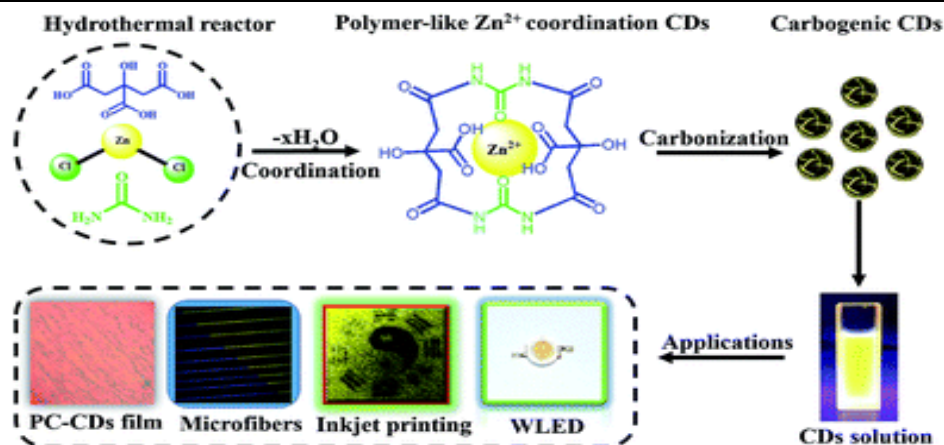


Fig. 10. Schematic illustrating the synthesis and the applications of the Zn-CDs.

5. Summary and perspectives

In this paper, the recent progress of M-CDs from the aspects of synthesis methods, novel physicochemical properties, and their applications have been discussed. More importantly, the as-prepared M-CDs not only exhibit high QYs but also endow excellent properties, which promises their potential applications in various fields including sensors, bioimaging, phototherapy, and beyond. However, there are several aspects that remain to be debated because the research on M-CDs is still at its early stage.

First of all, the physicochemical properties of M-CDs are related to their structure, composition, surface chemistry, and the available synthetic routes of M-CDs. Therefore, it is urgent to improve synthetic methods for the preparation of M-CDs via varying the kinds and dosage of metallic dopants and carbon sources, as well as combining two or more synthetic methods under different conditions. Secondly, the detailed photoluminescence mechanism and the relationship between the doping metal ions and the QYs improvement of M-CDs are ambiguous; therefore, a systematic study should be carried out to provide the experimental foundation and theoretical basis for the further study of M-CDs. Thirdly, more novel physicochemical properties should be explored. Since M-CDs also endow excellent optical and electronic properties, most metal ions display different valences, thus, M-CDs might possess CL and ECL, especially in the systems with redox reactions. Last but not least, although doping metal ions leading to the higher QYs and the good biocytotoxicity of M-CDs have been verified, it should be considered that some metal ions are harmful to organisms at high concentrations. Besides, more application fields of M-CDs should be explored such as, pollutant detection, drug delivery and release, bacteriostasis, cell tracing, and beyond.

REFERENCES

- [1] X. Xu et al, "Electrophoretic analysis and purification of fluorescent single-walled carbon nanotube fragments," *J. Am. Chem. Soc.*, vol.126, no.40, pp. 12736–12737, 2004.
- [2] S.Y. Lim et al, "Carbon quantum dots and their applications," *Chem. Soc. Rev.*, vol. 44, no.1, pp. 362–381, 2015.
- [3] S. Zhu et al, "Highly photoluminescent carbon dots for multicolor patterning, sensors, and bioimaging," *Angew. Chem. Int. Ed.*, vol.52, no.14, pp. 3953–3957, 2013.
- [4] S.N. Baker et al, "Luminescent carbon nanodots: emergent nano lights," *Angew Chem. Int. Ed. Engl.*, vol.49, pp. 6726–6744, 2010.
- [5] P. Miao et al, "Recent advances in carbon nanodots: synthesis, properties, and biomedical applications," *Nanoscale*, vol.7, pp. 1586–1595, 2015.
- [6] X.H. Gao et al, "Carbon quantum dot-based nanoprobes for metal ion detection," *J. Mater. Chem. C*, vol.4, pp. 6927–6945, 2016.
- [7] H.J. Sun et al, "Recent advances in graphene quantum dots for sensing," *Mater. Today*, vol.16, pp. 433–442, 2013.
- [8] J. Zhang et al, "Carbon dots: large-scale synthesis, sensing, and bioimaging," *Mater. Today*, vol.19, pp. 382–393, 2016.
- [9] X.T. Zheng et al, "Glowing graphene quantum dots and carbon dots: properties, syntheses, and biological applications," *Small*, vol.11, pp. 1620–1636, 2015.
- [10] F.L. Yuan et al, "Shining carbon dots: synthesis and biomedical and optoelectronic applications," *Nano Today*, vol.11, pp. 565–586, 2016.
- [11] Y. Du et al, "Chemically doped fluorescent carbon and graphene quantum dots for bioimaging, sensor, catalytic and photoelectronic applications," *Nanoscale*, vol.8, pp. 2532–2543, 2016.

- [12] Y.-P. Sun et al, "Doped carbon nanoparticles as a new platform for highly photoluminescent dots," *J. Phys. Chem. C*, vol.112, no.47, pp. 18295–18298, 2008.
- [13] Y. Wang et al, "Functionalization of carbonaceous nanodots from Mn(II)-coordinating functional knots," *Chem. Eur J.*, vol. 21, no.42, pp. 14843–14850, 2015.
- [14] K.Q. Wang et al, "Effects of elemental doping on the photoluminescence properties of graphene quantum dots," *RSC Adv.*, vol.6, pp.91225–91232, 2016.
- [15] Q. Xu et al, "Heteroatom-doped carbon dots: synthesis, characterization, properties, photoluminescence mechanism and biological applications," *J. Mater. Chem. B*, vol.4, pp. 7204–7219, 2016.
- [16] F. Li et al, "Non-metal-heteroatom-doped carbon dots: synthesis and properties," *Chem. Eur. J.*, vol.25, pp. 1165–1176, 2019.
- [17] M.L. Liu et al, "Carbon dots: synthesis, formation mechanism, fluorescence origin, and sensing applications," *Green Chem.*, vol.21, pp. 449–471, 2019.
- [18] L.P. Lin et al, "Metal ions doped carbon quantum dots: Synthesis, physicochemical properties, and their applications," *Trends Anal. Chem.*, vol.103, pp. 87–101, 2018.
- [19] M.Z. Zhang et al, "When rare earth meets carbon nanodots: mechanisms, applications and outlook," *Chem. Soc. Rev.*, vol.49, pp. 9220–9248, 2020.
- [20] X. Li et al, "Metal ions-doped carbon dots: Synthesis, properties, and applications," *Chem. Eng. J.*, vol.430, 133101, 2022.
- [21] Y. Liu et al, "Yellow emissive carbon dots with quantum yield up to 68.6% from manganese ions," *Carbon*, vol.135, pp. 253–259, 2018.
- [22] M.X. Yang et al, "Facile synthesis of Mg²⁺-doped carbon dots as novel biomaterial inducing cell osteoblastic differentiation," *Part. Part. Syst. Charact.*, Vol.36, 1800315, 2019.
- [23] Q. Xu et al, "Highly fluorescent Zn-doped carbon dots as Fenton reaction-based bio-sensor: An integrative experimental-theoretical consideration," *Nanoscale*, vol.8, pp.17919–17927, 2016.
- [24] Y. Huang et al, "Gadolinium-doped carbon quantum dots loaded magnetite nanoparticles as a bimodal nanoprobe for both fluorescence and magnetic resonance imaging," *Magn. Reson. Imaging*, vol.68, pp. 113–120, 2020.
- [25] H.-Y. Zhang et al, "Rapid detection of Cr (VI) ions based on cobalt(II)-doped carbon dots," *Biosens. Bioelectron.*, vol.87, pp. 46–52, 2017.
- [26] S.J. Zhuo et al, "One-step hydrothermal synthesis of silver doped carbon quantum dots for highly selective detection of uric acid," *Methods Appl. Fluoresc.*, vol.8, 015005, 2020.
- [27] C.M. Li et al, "Chromium (III)-doped carbon dots: fluorometric detection of p-nitrophenol via inner filter effect quenching," *Microchim. Acta*, vol.186, pp. 384–392, 2019.
- [28] Q. Xu et al, "Facile synthesis of copper doped carbon dots and their application as a "turn-off" fluorescent probe in the detection of Fe³⁺ ions," *RSC Adv.*, vol.6, pp. 28745–28750, 2016.
- [29] T. Liu et al, "Fluorescence detection of mercury ions and cysteine based on magnesium and nitrogen co-doped carbon quantum dots and implication logic gate operation," *Sensor. Actuat. B: Chemical*, vol.231, pp. 147–153, 2016.
- [30] W.Q. Yang et al, "High peroxidase-like activity of iron and nitrogen co-doped carbon dots and its application in immunosorbent assay," *Talanta*, vol.164, pp. 1–6, 2017.
- [31] N.Q. Gong et al, "Microwave-assisted polyol synthesis of gadolinium-doped green luminescent carbon dots as a bimodal nanoprobe," *Langmuir*, vol.30, pp. 10933–10939, 2014.
- [32] Y. Chen et al, "Enhanced photoluminescence properties of carbon dots by doping with europium," *J. Nanosci. Nanotechnol.*, vol.16, pp. 3735–3738, 2016.
- [33] W.T. Wu et al, "Cu-N dopants boost electron transfer and photooxidation reactions of carbon dots," *Angew Chem. Int. Ed. Engl.*, vol.54, pp. 6540–6544, 2015.
- [34] L. Wang et al, "Versatile self-assembly and biosensing applications of DNA and carbon quantum dots coordinated cerium ions," *Chem. Eur J.*, vol.23, pp. 10413–10422, 2017.
- [35] B.B. Chen et al, "Highly selective detection of 2,4,6-trinitrophenol by using newly developed terbium-doped blue carbon dots," *Analyst*, vol.141, pp. 2676–2681, 2016.
- [36] K. Bera et al, "Metamorphosis of ruthenium-doped carbon dots: in search of the origin of photoluminescence and beyond," *Chem. Mater.*, vol.28, pp. 7404–7413, 2016.
- [37] Q.G. Zhang et al, "Graphene structure boosts electron transfer of dual-metal doped carbon dots in photooxidation," *Carbon*, vol.126, pp. 128–134, 2018.
- [38] A.B. Bourlinos et al, "Fe(III)-functionalized carbon dots-highly efficient photoluminescence redox catalyst for hydrogenations of olefins and decomposition of hydrogen peroxide," *Appl. Mater. Today*, vol.7, pp. 179–184, 2017.
- [39] L. Wang et al, "Gadolinium-doped carbon dots with high-performance in dual-modal molecular imaging," *Anal. Methods*, vol.13, no.21, pp. 2442–2449, 2021.
- [40] J. Li et al, "A novel N/Au co-doped carbon dot probe for continuous detection of silicate and phosphate by resonance Rayleigh scattering," *Analyst*, vol.144, 5090, 2019.
- [41] H.L. Dong et al, "Microwave-assisted polyol synthesis of water dispersible red-emitting Eu³⁺-modified carbon dots," *Mater.*, vol.10, pp. 25–34, 2016.
- [42] W. Yang et al, "High peroxidase-like activity of iron and nitrogen co-doped carbon dots and its application in immunosorbent assay," *Talanta*, vol.164, pp. 1–6, 2017.
- [43] S.K. Tammina et al, "Synthesis of N, Zn-doped carbon dots for the detection of Fe³⁺ ions and bactericidal activity against Escherichia coli and Staphylococcus aureus," *J. Photochem. Photobiol. B*, vol.202, 111734, 2020.
- [44] H.M. Chen et al, "Mesoporous silica as nanoreactors to prepare Gd-encapsulated carbon dots of controllable sizes and magnetic properties," *Adv. Funct. Mater.*, vol.26, pp. 3973–3982, 2016.

- [45] L.P. Lin et al, "Europium-decorated graphene quantum dots as a fluorescent probe for label-free, rapid and sensitive detection of Cu²⁺ and L-cysteine," *Anal. Chim. Acta*, vol.891, pp. 261–268, 2015.
- [46] C. Zhu et al, "Deep ultraviolet emission photoluminescence and high luminescence efficiency of ferric passivated graphene quantum dots: strong negative inductive effect of Fe," *Synthetic Met.*, vol.209, pp. 468–472, 2015.
- [47] M.D. Xu et al, "Terbium ion-coordinated carbon dots for fluorescent aptasensing of adenosine 5'-triphosphate with unmodified gold nanoparticles," *Biosens. Bioelectron.*, vol.86, pp. 978–984, 2016.
- [48] M.L. Liu et al, "One-pot carbonization synthesis of europium-doped carbon quantum dots for highly selective detection of tetracycline," *Methods Appl. Fluoresc.*, vol.5, 015003, 2017.
- [49] Z.X. Liu et al, "Cu(I)-doped carbon quantum dots with zigzag edge structures for highly efficient catalysis of azide-alkyne cycloadditions," *Green Chem.*, vol.19, pp. 1494–1498, 2017.
- [50] Y.H. Yuan et al, "Germanium-doped carbon dots as a new type of fluorescent probe for visualizing the dynamic invasions of mercury(II) ions into cancer cells", *Nanoscale*, vol.7, pp. 16841–16847, 2015.
- [51] Y. Pan et al, "One-pot synthesis of gadolinium-doped carbon quantum dots for high-performance multimodal bioimaging," *J. Mater. Chem. B*, vol.5, pp. 92–101, 2017.
- [52] C.P. Han et al, "Synthesis of a multifunctional manganese(II)-carbon dots hybrid and its application as an efficient magnetic-fluorescent imaging probe for ovarian cancer cell imaging," *J. Mater. Chem. B*, vol.4, pp. 5798–5802, 2016.
- [53] X.Y. Ren et al, "Facile preparation of gadolinium(III) chelates functionalized carbon quantum dot-based contrast agent for magnetic resonance/fluorescence multimodal imaging," *J. Mater. Chem. B*, vol.2, pp. 5541–5549, 2014.
- [54] Y. Xu et al, "Carbon quantum dot stabilized gadolinium nanoprobe prepared via a one-pot hydrothermal approach for magnetic resonance and fluorescence dual-modality bioimaging," *Anal. Chem.*, vol.86, pp. 12122–12129, 2014.
- [55] Z. Shen et al, "Microwave-assisted synthesis of cyclen functional carbon dots to construct a ratiometric fluorescent probe for tetracycline detection," *J. Mater. Chem. C*, vol.6, no.36, pp. 9636–9641, 2018.
- [56] X. Li et al, "Advances and perspectives in carbon dot-based fluorescent probes: Mechanism, and application," *Coord. Chem. Rev.*, vol.431, 213686, 2021.
- [57] M. Hu et al, "Highly sensitive detection of glucose by a "Turn-Off-On" fluorescent probe using gadolinium-doped carbon dots and carbon microparticles," *J. Biomed. Nanotechnol.*, vol.14, no.6, pp. 1117–1124, 2018.
- [58] B. Wang et al, "Osteogenic potential of Zn²⁺-passivated carbon dots for bone regeneration in vivo," *Biomater. Sci.*, vol.7, no.12, pp. 5414–5423, 2019.
- [59] R. Kumari et al, "pH-responsive Mn-doped carbon dots for white-light-emitting diodes, fingerprinting, and bioimaging," *ACS Appl. Nano Mater.*, vol.2, no.9, pp. 5900–5909, 2019.
- [60] F. Du et al, "Engineered gadolinium-doped carbon dots for magnetic resonance imaging-guided radiotherapy of tumors," *Biomaterials*, v.121, pp. 109–120, 2017.
- [61] J. Dong et al, "Unique effect of Cu (II) in the metal-induced amyloid formation of β -2-microglobulin," *Biochem.*, vol.53, no.8, pp. 1263–1274, 2014.
- [62] M. Lin et al, "Cu(II) doped polyaniline nanoshuttles for multimodal tumor diagnosis and therapy," *Biomater.*, vol.104, pp.213–222, 2016.
- [63] X.-L. Guo et al, "A novel strategy of transition-metal doping to engineer absorption of carbon dots for near-infrared photothermal/photodynamic therapies," *Carbon*, vol.134, pp. 519–530, 2018.
- [64] T.H. Kim et al, "Yellow-emitting carbon nanodots and their flexible and transparent films for white LEDs," *ACS Appl. Mater. Interfaces*, vol.8, no.48, pp. 33102–33111, 2016.
- [65] Y.L. He et al, "Double carbon dot assembled mesoporous aluminas: solid-state dual-emission photoluminescence and multifunctional applications," *J. Mater. Chem. C*, vol.6, pp. 2495–2501, 2018.
- [66] J. Cheng et al, "Zinc ion-doped carbon dots with strong yellow photoluminescence," *RSC Adv.*, vol.6, pp. 37189–37194, 2016.



Dang Dinh Khoi was born on 18th October 1975 in Ca Mau City, the foremost south of Vietnam. He received a B.S. degree in Chemical and Food Technology in 1998 and an M.Sc. degree in Chemical Engineering in 2006, both from Ho Chi Minh City University of Technology, Ho Chi Minh City, Vietnam. From 2013 to 2018, he studied at the School of Chemical Engineering, University of Ulsan, Ulsan, South Korea as a Ph.D. student. He earned his Ph.D. degree in Chemical Engineering in February 2018.

He is now working as a Post-Doctoral Researcher in the Semiconductor Devices Research Lab, Energy Harvest-Storage Research Center, Research Institute for Natural Science, Department of Physics, University of Ulsan, South Korea. In 2019 he joined the Department of Chemical Technology, Faculty of Chemical and Food Technology, Ho Chi Minh City University of Technology and Education, Vietnam. His current scientific interests are carbon dots, fluorescent nanomaterials, and their applications include chemical sensing, bioimaging, and Light-Emitting Diodes (LEDs).



Pham Thanh Tung received a B.S. degree in Food Science and Technology from Nong Lam University, Ho Chi Minh City, Vietnam, in 2015 and an M.S. degree in Product Development from Kasetsart University, Bangkok, Thailand, in 2018. He is currently pursuing a Ph.D. degree in Food Science at the Hungarian University of Agriculture and Life Sciences, Budapest, Hungary.

Since 2019 he is a Lecturer at the Department of Food Technology, Faculty of Chemical and Food Technology, Ho Chi Minh City University of Technology and Education, Vietnam. His research interest includes starch, fiber, and the development of products related to them.