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Nanomaterials as a new frontier platform: metal-doped and hybrid carbon dots as enzyme mimics for environmental applications

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Environmental pollution has become an inexorable problem for the planet Earth. The precise detection and degradation of heavy metals, pesticides, industrial-, pharmaceutical- and personal care- products is needed. Nanotechnology holds great promise in addressing global issues. Over the past decades, nanozymic nanomaterials have exceptionally overcome the intrinsic limitations of natural enzymes. Carbon dots (CDs) exhibit unique structures, surface properties, high catalytic activities, and low toxicity. Different techniques, such as doping or surface passivation, can enhance these exceptional properties. Doping modifies CDs' electronic, magnetic, optical, and catalytic properties considerably. Metal doping, a more significant strategy, involves the introduction of metallic impurities, which offer insight into enhancing the physicochemical properties of CDs. Metal-doped CDs exhibit higher optical absorbance and catalytic performance than pristine CDs. The literature shows that researchers have utilized various synthetic approaches to fabricate CDs-Metal nanozymes. Researchers have reported the metal-doped and hybrid CDs' peroxidase, catalase, laccase, and superoxide dismutase-like activities. These metal-doped nanozymes put forward substantial environmental remediations and applications such as sensing, photocatalytic degradation, adsorption, and removal of environmental contaminants. This review thoroughly discussed the metal-based functionalization of CDs, the enzyme-like properties, and the ecological applications of metal-doped and hybrid enzymes. The review also presents the current novelties, remaining challenges, and future directions with key examples.

KEYWORDS

carbon dots, robust materials, functional attributes, efficient catalysis, enzyme mimics, remediation

1 Introduction

The environment is essential for sustaining life, but environmental pollution causes alarming obstacles to the viability of Earth. Several anthropogenic practices, such as industrialization, agriculture, and transportation, have been the leading cause of environmental contamination (Awewomom et al., 2024; Ukaogo et al., 2020). Such contamination eventually leads to ecological, health, and economic consequences. Regarding health issues, cancer, respiratory problems, and numerous chronic diseases are caused by chemical pollutants (Kim et al., 2018). However, global efforts are steadily being made to alleviate environmental pollution and protect human health. Nanotechnology is an advanced field unveiling significant ecological protection (Khin et al., 2012). Owing to their ultra-compact size, high surface area, non/less toxicity, and easy biodegradation, carbon nanomaterials are considered valuable (Liu Y. et al., 2020; Choudhary et al., 2014; Cao et al., 2013). The advancement of carbon dots has attracted attention in the crossover field of carbon materials and pristine quantum dots.

Carbon dots (CDs), the quasi-spherical, zero-dimensional competitive members (less than 10 nm in size), belong to the family of carbon nanomaterials (Sagbas and Sahiner, 2019; Zhao Q. et al., 2020; Cui et al., 2021; Langer et al., 2021). In 2004, CDs were accidentally discovered during the purification of single-walled nanotubes (SWNTs) using an arc discharge method. Thereafter, the research on CDs rapidly increased. CDs exhibit small size, larger surface-to-volume area, active edges, fluorescent properties, strong absorption, resistance to photo-decomposition, low toxicity, biocompatibility, and enhanced catalytic activity (Figure 1; Zhang et al., 2021; Innocenzi and Stagi, 2023; Ge et al., 2018; Chen et al., 2021). Carbon, hydrogen, and oxygen are the main constituents of CDs. The carbon core consisting of crystalline sp^2 carbon comprises amino ($-NH_2$), hydroxyl (-OH) and carboxyl (-COOH) groups.

CDs are diverse, and are further classified. Each class's size, properties, structure, and formation mechanism may vary. Graphene Quantum Dots (GQDs), Polymer Dots (PDs), and Carbon Nanodots (CNDs) are the main categories. The CNDs exhibit amorphous spherical morphology (Pathak et al., 2023). Their core contains a high degree of carbonization (Langer et al., 2021). CNDs bifurcates into Carbon Quantum Dots (CQDs) and Carbon Nanoparticles (CNPs). The amorphous CNPs do not exhibit Quantum Confinement Effect (QCE), while the CQDs having surface chemical groups and graphene-layer show QCE (Ozyurt et al., 2023; Bacon et al., 2014). GQDs have significant properties and are excellent fluorophores and electro-catalysts (Mansuriya and Altintas, 2020; Ghaffarkhah et al., 2022). GQDs may show the QCE. The last type, polymer dots (PDs), comprise low carbonization; they have either linear polymers or monomers grouping (Ozyurt et al., 2023; Song et al., 2017). Different methods have been employed for their synthesis, such as chemical oxidation, microwave-assisted synthesis, laser ablation, atmospheric plasma-based synthesis, thermolysis, hydrothermal carbonization, solvothermal, electrochemical, and ultrasonic methods. Among all these synthetic techniques, the solvothermal method (particularly hydrothermal) is commonly used to synthesize doped CDs.

Despite the unique physicochemical properties of CDs, pristine CDs show some limitations, such as, low quantum yield and ease of contamination. Hence, extensive research has been conducted in improving and tailoring their functionality over the years. Doping has been widely utilized in optimizing CDs' intrinsic chemical, electrical and optical properties. Top-down and bottom-up approaches are the two main synthetic methods for reporting hetero-atom-doped CDs (Miao et al., 2020). The former approach majorly involves tailoring pre-existing carbonaceous material. In contrast, the bottom-up approach involves synthesizing material from the ground up. Compared to the top-down, the bottom-up approach allows precise manipulation of synthesis conditions and, hence, offers more control over CD material structure and properties (Alafeef et al., 2024).

Researchers have reported peroxidase, oxidase, superoxide dismutase, and catalase-like activity in functionalized CDs (Zhu et al., 2014; Wang H. et al., 2021; Wu et al., 2019; Zhang et al., 2023). These CDs exhibit excellent stability than natural enzymes and are utilized as enzyme alternatives for environmental applications (Gao et al., 2007). Like natural enzymes, their catalytic activity is sensitive to pH, temperature, and concentration. The peroxidase-like catalytic activity of CDs was first reported by Shi et al. (2011). Later, many other researchers synthesized doped and/or hybrid CDs (especially metal-doped CDs) to enhance the enzyme-mimicking activity of CDs (Lopez-Cantu et al., 2022). A comparative analysis between different metal-doped (including Ce-doped, Cr-doped, Cu-doped, Fe-doped, and Mn-doped CDs) and non-metal-doped CDs as peroxidase-mimics has also been reported (Yuxin et al., 2022). The results confirmed that both non-metal and metal-doped CDs exhibit peroxidase-like catalytic activity; however, the metal-doped CDs, such as Fe-doped CDs, show the highest catalytic activity and act as excellent artificial enzymes. In other words, the metal-doped CDs exhibit more catalytic active sites and improved binding selectivity (Gallareta-Olivares et al., 2023).

The fluorometric/colorimetric property of metal-doped and hybrid CDs for detecting chemical pollutants facilitates a sensitive monitoring system (Nejad et al., 2020). The common insecticide and high-risk water contaminant, *p*-nitrophenol (p-NP), has been detected through fluorometric Cr-doped CDs sensors (Li C. et al., 2019). Similarly, the hybrid nanozymic-nanoreactors based on Fe-doped CDs (Fe-CDs) and MOF-808 were reported to detect and degrade organophosphorus pesticides. The author also noted a synergistic effect of Fe-CDs on MOF-808-comprised complex to sense paraoxon and parathion (Ma et al., 2023). Similarly, Cu-doped Tragacanth/Chitosan CDs and Fe-doped N@CDs detect isoniazid (INH) and doxycycline (Shekarbeygi et al., 2020; Kaur et al., 2022a).

2 The structural/functional rationale CDs

Carbon Dots (CDs) are a class of zero-dimensional, quasi-spherical shaped nanomaterial having a usual size of less than 10 nm (Cui et al., 2021; Kurian and Paul, 2021). Researchers report that the surface area of CDs varies from 16.4 $m^2\ g^{-1}$ to 1,690 $m^2\ g^{-1}$ (Wang Q. et al., 2013; Ren et al., 2019). The carbon present in their structure is sp^2 and sp^3 hybridized. The sp^2/sp^3 carbons comprised of CDs attach many functional groups and polymer chains. Depending on the degree of carbonization, the

TABLE 1 Environmental Applications of CDs/Functionalized CDs and Metal doped and Hybrid CDs.

CDs/Metal doped and hybrid CDs	Analyte	Limit of detection (LOD)	Degradation*	Environmental application	Reference
CDs	Pretilachlor	2.9 μM	—	Detection of pretilachlor	Deka et al. (2019)
CDs	Diazinon Amicarbazone Glyphosate	0.25 ng/mL 0.5 ng/mL 2 ng/mL	—	Fluorescent sensing of pesticides	Ashrafi Tafreshi et al. (2020)
CDs	Diazinon	0.038 μM	—	Detection of diazinon in tap, distilled, and river water	Khaledian et al. (2021)
KCDs	Picric acid Cu^{2+} Fe^{3+}	86 ng/mL 15.3 mg/mL 0.36 μg/mL	—	Removal of alkaline and organic impurities from wastewater	Venkatesan et al. (2019)
YCDs	2,4,6-trinitrophenol (TNP)	56 nM	—	Sensitive detection of TNP in environmental samples	Zhang et al. (2020a)
Y-CDs	Cr (VI)	4.5 μM	—	Detection of Cr (VI) in water samples	Zhang et al. (2020b)
GHS-CDs	As^{3+} ClO^{-}	2.3 nM 0.016 μM	—	Sensing of As^{3+} and ClO^{-} in drinking water	Radhakrishnan and Panneerselvam (2018)
PDA@CDs	*p*-Chlorophenol (*p*-CP) *p*- Cyanophenol (*p*-CNP)	—	153 mg/g 178 mg/g	Absorption of phenolic compounds in wastewater	Sanni et al. (2022)
PC-CDs	Cu^{2+}	0.05 μg/mL	—	Detection of Cu^{2+} in wastewater samples	
FCDs	Tetracycline (TC)	0.005 mg/L	—	Detection of TC in sewage water	Guo et al. (2020)
NCDs/g-C3N4	Oxytetracycline (OTC)	—	91.2% in 24 h	Degradation of OC in aquaculture wastewater	Peng et al. (2024)
CDs/MnO_2 assembly	Hydrazine	4.8 ppb	—	Sensitive detection of hydrazine from water	Hiremath et al. (2020)
Fe^{2+}-CDs	Histidine Zn^{2+}	10 μM 0.1 μM	—	Detection of Histidine and Zinc ions in water samples	Han et al. (2018)
Fe-N@CDs	Doxycycline	66 ngml/L	—	Detection and degradation of doxycycline	Kaur et al. (2022b)
Fe_3O_4-CDs	Doxycycline	—	70.26% in 5 min	Degradation of doxycycline	Kaur et al. (2022b)
CCDs (Co (II) doped CDs)	Cr (VI)	1.17 μM	—	Sensing of Cr (VI) ions in tap water	Zhang et al. (2017a)
GT/CS/Cu	Isoniazid	0.0011 μg.ml/L	—	Detection of isoniazid in wastewater samples	Shekarbeygi et al. (2020)
Ni-CQDs	Fe^{3+} Cu^{2+}	10.17 μM 7.88 μM	—	Metals ion detection	Sun et al. (2023a)
CDs/Cu	Thiophanate methyl (TM)	2.908×10^{-6} mol/L	—	Fluorescent sensing of TM pesticide	Han et al. (2019)

(Continued on the following page)

TABLE 1 (*Continued*) Environmental Applications of CDs/Functionalized CDs and Metal doped and Hybrid CDs.

CDs/Metal doped and hybrid CDs	Analyte	Limit of detection (LOD)	Degradation*	Environmental application	Reference
Cu,N-CDs/Ag3PO4	Neutral Red (NR)	—	69.7% in 60 min	Degradation of NR from wastewater	Mu et al. (2019)
CDs/ZFO	Methyl Orange (MO)	—	—	Removal of organic dye MO from water	Shi et al. (2018)
CDs/ZFO	Tetracycline (TC)	—	(under visible light) 79.5% in 120 min	Photocatalytic degradation of TC from wastewater	Shi et al. (2022)
NPCQD/ZnO	Methylene Blue (MB)	—	90% in 30 min	Photodegradation of MB from wastewater	Song et al. (2019)
(CDs)/g-C_3N_4/ZnO	Tetracycline (TC)	—	100% in 30 min	Photocatalytic degradation of TC	Guo et al. (2017)
Mg,N-CDs	Paraoxon	0.87 nM	181.2 mg/g	Detection of paraoxon in tap and river water	Peng et al. (2019)
CDs-TGA-CdTe	Chlortoluron	7.8×10^{-11} mol/L	—	Analysis of chlortoluron in irrigation water samples	Tao et al. (2015)
CQD-AuNPs	Paraoxon Malathion Methamidophos Carbaryl	0.05 nM 0.10 nM 0.12 nM 0.13 nM	—	Detection of pesticides in tap and river water	Korram et al. (2019)
CDs-AgNPs	Phoxim	40 nM	—	Detection of phoxim in environmental water samples	Zheng et al. (2018)
AuNPs and CQDs	Carbaryl	0.06 μg/L	—	Detection of carbaryl in real water samples	Chen et al. (2020)
AuNPs and CDs	Acetamiprid	1.5×10^{-9} mol/L	—	Detection of acetamiprid	Qin et al. (2019b)

*Expressed like (% and time)/Absorbance (mg/g).

sp^2/sp^3 carbon-skeleton shows an amorphous-form or a graphite-lattice (Mansuriya and Altintas, 2021). Relative to Quantum Dots and other nanomaterials, CDs are functionally less toxic, highly luminescent, biocompatible, inexpensive, and thermally stable. Regarding Photoluminescence (PL) studies, they show dispersion, UV-vis absorption, quantum yield, and phosphorescence. They also exhibit core-state emission, molecular fluorescence, and surface-state emission (Li Z. et al., 2019). Despite the advanced applications of CDs, few of the fundamental properties of CDs are still uncertain. Such uncertainties hinder scientists from enhancing CDs' properties and applications for future visions (Mintz et al., 2021). Figure 2 shows the characteristic description of CDs' morphological and photoluminescent features.

CDs offer several beneficial properties due to functional groups on the surface. These functional groups also impart catalytic activity to CDs. Both reducing and oxidizing species can be used to synthesize CDs. As a result, CDs can lead the redox transformation reactions (Mokoloko et al., 2023). These redox reactions give rise to many applications in pollution control, industrial catalysis, waste treatment, and degradation of pharmaceuticals (Tarumi et al., 2019; Toral-Sánchez et al., 2018). Moreover, the functional groups are highly significant in enhancing the properties of CDs in biosensing and molecule detection. Yan et al. reported that CDs' properties could be improved by modification procedures in which the covalent or non-covalent bonding is built between the reactants and the CD surface. Studies show that two different CDs can react to a new CD, exhibiting the surface properties of both parent CDs. Similarly, three other types of CDs were produced by Zhou. et al. The reaction was kept at room-temperature conditions, and reactant CDs formed a link between their functional groups. CDs formed in products were utilized as nanocarriers in drug delivery systems (Mokoloko et al., 2023).

Hydrophilic and hydrophobic groups on CDs enhance their solubility and stability in water and organic solvents (Li Z. et al., 2019; Mokoloko et al., 2023). The hydrophobicity and hydrophilicity of CDs can be altered by using precursors and passivators (Rui et al., 2023). For Bioimaging and NIR-Anticounterfeiting the hydrophobic CDs have been utilized (Shi et al., 2023). Hydrophilic CDs act as metal-ion detectors and fluorescent pH sensors (Liu X. et al., 2018). The hydrophilic properties of CD

TABLE 2 Hydrothermally synthesized Metal Doped and Hybrid Carbon Dots involved in Environmental Remediation.

Metal doped/hybrid CDs	Autoclave conditions	Metal precursor	Carbon precursor	Analyte	Properties	Reference
Cr-CDs	200°C, 12 h	Tris (acetylacetonato)chromium	Polyethyleneimine	*p*-Nitrophenol (*p*-NP)	Crystalline, uniform in size, highly fluorescent	Li et al. (2019a)
Fe-CDs	180°C, 10 h	Iron (II) chloride hexahydrate	Ethylenediaminetetraacetic acid disodium salt (EDTA-2Na)	CO_2	Spherical, narrow size distribution, improved photocatalytic performance	Dang et al. (2023)
Ni-CDs	160°C, 8 h	Nickel sulfate hexahydrate	Citric acid	Urea	1.62 nm diameter, 1.56 nm particle size, excellent catalytic activity	Zhu et al. (2023)
Cu-CDs and CuCys-CDs	180–200°C, 5–10 h	Copper (II) nitrate	Polyethylene glycol, L-cysteine	Methyl orange (MO), Orange II sodium salt (O-II), Reactive Black 5 (RB-5), Remazol Brilliant Blue R (RBB-R)	Spherical, 4.0 nm size, high QY, exhibit catalytic ozonation activity	Cardoso et al. (2022)
Cu-CDs	Constant, 5–9 h	Copper (II) nitrate	Poly (methacrylic acid sodium salt)	p-phenylenediamine (PPD), Hydroquinone (HQ)	Near-spherical, laccase-like activity, fluorescent, exhibit photostability	Ren et al. (2015)
Cu-CDs	180°C, 10 h	Copper (II) chloride dihydrate	Ethanediamine	*p*-Nitrophenol (*p*-NP)	1.8 nm average diameter, fluorescent, excellent selectivity and sensitivity	Fang et al. (2019)
Zn-CDs	185°C, 1–10 h	Zinc chloride	Sodium citrate	Hg^{2+}	Quasi-spherical, diameter less than 3 nm, luminescent	Xu et al. (2018)
N/AL-CDs	210°C, 12 h	Aluminum nitrate	Durian shell waste (DSW)	Mn^{7+}	Quasi-spherical, 10.0 nm average diameter, excellent selectivity and sensitivity	Jayaweera et al. (2019)
CDs/Cu	180°C, 4 h	Copper chloride	1-(2-Pyridylazo)-2-naphthol	Thiophanate methyl (TM)	5.78 nm average diameter, enhanced selectivity	Han et al. (2019)
GT/CS/Cu-based CDs	250°C, 45 min	Copper (II) sulfate	Biopolymers; Gum Tragacanth (GT) and Chitosan (CS)	Isoniazid	spherical, 6.2 nm particle size, fluorescent	Shekarbeygi et al. (2020)
Ag-CDs	120°C, 4 h	Silver nitrate	Polyethyleneimine	$Cr_2O_7^{2-}$	2.6–6.0 nm diameter, fluorescent, multifunctional	Hu et al. (2020)
Bi-RHCQDs (Bismuth-doped rice husk-derived CDs)	190°C, 4 h	Bismuth nitrate pentahydrate	Rice husk	Methyl blue (MB), Cu (II) ions	Around 4.892 nm particle diameter	Hui et al. (2021)

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TABLE 3 Enzyme mimetic metal-doped and hybrid carbon dots.

Metal-doped CD-based nanozymes	Synthetic approach	Metal precursor	Carbon precursor	Enzyme-like activity	Reference
Cu-CDs	Solid-phase	Copper (II) nitrate trihydrate	Citric acid	Peroxidase	Duan et al. (2019)
Fe-N-CDs	Solvothermal	Iron (III) chloride hexahydrate	Tartaric acid	Peroxidase	Yang et al. (2017)
Fe,N-CDs	Hydrothermal	Anhydrous ferric chloride	Histidine	Peroxidase	Xu et al. (2023)
N, Fe-CDs	Hydrothermal	Iron (III) chloride hexahydrate	β-cyclodextrin	Peroxidase	Li et al. (2020c)
Co, N-CDs	Hydrothermal	Vitamin B_{12}	Vitamin B_{12}	Oxidase	Hu et al. (2024)
Mn-CDs	Hydrothermal	Manganese (II) chloride tetrahydrate	Citric acid, ethylenediamine	Oxidase	Zhuo et al. (2019)
N, Cu-CDs	Hydrothermal	Copper (II) nitrate trihydrate	EDTA	Peroxidase	Lin et al. (2019)
Fe/N@C-dots	Hydrothermal	Iron (III) chloride hexahydrate	Na_2EDTA	Peroxidase	Alqahtani et al. (2023)
Fe@Fn-CDs	Hydrothermal	Ferrous cation (Fe^{2+})	Horse spleen apoferritin	Peroxidase, Oxidase, Catalase, Superoxide Dismutase	Shen et al. (2023)
4-ASA/Gd-CDs	Hydrothermal	Gadolinium cation (Gd^{3+})	Polyethyleneimine (PEI)	Superoxide dismutase	Zhao et al. (2024)
(Fe,Co) codoped-CDs	Hydrothermal	Iron (III) chloride hexahydrate, Cobalt (III) chloride hexahydrate	Citric acid	Peroxidase	Li et al. (2021b)

surface also offer several applications in medicinal chemistry (Jana and Dev, 2022). Moreover, CDs can also be used to modify several reactions (Mokoloko et al., 2023).

CDs carry photocatalytic processes in environmental applications. CDs-based photocatalysis works in the degradation of pollutants and energy conversion as well. Carbon allotropes have been used in titania-supported photocatalysis in the past few years (Nguyen et al., 2015). The researchers have demonstrated the degradation of Tetracycline through titania nanoparticles-based photocatalysis (Zhu et al., 2013). Moreover, the metal-doped nanoparticles (NPs) increase light absorption properties by interacting incident photons with metal NPs electrons (Yao et al., 2022; Jana et al., 2016). This interaction is referred to as the Surface Plasmon Resonance Effect. CDs comprise ease in their functionalization (Gallareta-Olivares et al., 2023). The chemical and physical properties of CDs are enhanced and adjusted through Doping. Moreover, the doped-CDs have different energy gaps and electron densities than the un-doped ones (Li X. et al., 2022). The choice of dopant element is significant in obtaining desired features. Compared to non-metallic ions, metal ions have large atomic radii, more electrons, and unoccupied orbitals (Li X. et al., 2022). For these reasons, metal-doped CDs show excellent performance in bioimaging, biocatalysis, photocatalysis, and phototherapy (Boakye-Yiadom et al., 2019).

3 The physicochemical properties and functional elements

CDs show unique physical properties, i.e., high reactivity, good chemical reactivity, surface functionality, biocompatibility, hydrophilicity, electroconductivity, and low toxicity (Miao et al., 2020; Ranjan et al., 2022; Fawaz et al., 2023). The high reactivity of CDs can be justified by their smaller size, well-defined shapes, greater surface area, and integrated functional groups. Preference to reactive precursors and particular synthetic approaches can also significantly improve the reactivity (Papaioannou et al., 2019). The existence of different functional groups attached to the surface of CDs is referred to as surface and structural functionality (Figure 3). Such functional groups greatly influence other physicochemical properties. Surface functionality can originate from surface functionalization or precursors utilized in the synthesis (Yan et al., 2018). Hydroxy (-OH), amino (-NH_2), and carboxy (-COOH) groups are the most familiar

TABLE 4 Environmental applications of enzyme mimetic metal doped/hybrid carbon dots.

Metal doped/hybrid CDs	Enzyme-like activity	Environmental application	Reference
Cu-CDs	Laccase	Removal of phenylenediamine contaminant in environmental water samples	Ren et al. (2015)
Cu,Cl-CDs	Peroxidase, Oxidase	Detection of Hydroquinone in environmental water samples	Zhao et al. (2022)
Zn/Cl-CQDs	Peroxidase	Cu^{2+} detection in drinking water samples	Dadkhah et al. (2022)
NA-CDs/AuNPs	Peroxidase	Detection of methylmercury in environmental water samples	Li et al. (2023b)
CDs@Cu_4O_3	Peroxidase, Oxidase	Organic pollutants degradation	Li et al. (2020b)
CeO_2/N-CQDs@CuO NPs	Oxidase	Cr (VI) detection in real water samples	Qiu et al. (2024)
Co@CDs hybrid material	Peroxidase	Water treatment against methylene blue contaminant	Guo et al. (2015)
N/Cl-CDs and N/Cu-CDs system	Peroxidase	Determination of Hydroquinone in environmental water samples	Wang et al. (2020)

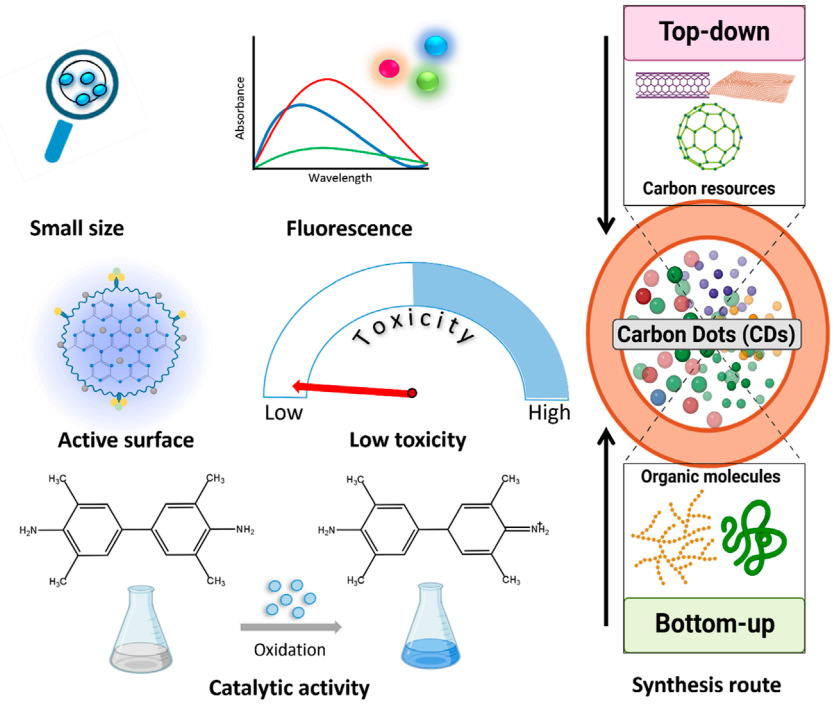


FIGURE 1
Physiochemical characteristics and optical attributes of Carbon dots (CDs).

functional groups found on CDs. The oxygenated functional groups, more specifically, affect the photoluminescence properties. Characteristic CDs, designed through surface modification, can further aid in developing multifunctional fluorescent probes for different purposes (Liu et al., 2016).

CDs' tailorable hydrophilic and hydrophobic properties are also promising in developing more advanced biological and environmental applications (Ozyurt et al., 2023; Zhang et al., 2024; Zhao and Zhu, 2018; Liu J. et al., 2020). Hydrophilicity provides stability to CDs in aqueous media, enhancing dispersion. Utilization

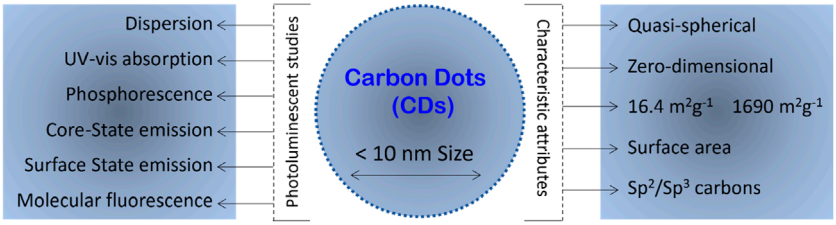


FIGURE 2
Characteristic attributes and photoluminescent features of carbon dots (CDs).

of ionic liquids (ILs), surface functionalization, and control of terminal alkyl chain length are a few of the significant methods involved in tuning the hydrophilicity of CDs (Ozyurt et al., 2023; Guo et al., 2019; Varisco et al., 2017; Guo et al., 2021; Zheng et al., 2019). In surface functionalization, hydrophilic functional groups such as -OH, -COOH, and -HN_3 are introduced on the CDs surface (Zhang et al., 2024; Zhao and Zhu, 2018). ILs (such as 1-alkyl-3-methylimidazolium dicyanamide) have been reported to synthesize both hydrophilic and hydrophobic CDs (Guo et al., 2019). Moreover, the amphiphilic carbon dots (ACDs) exhibit hydrophilic and lipophilic properties (Nandi et al., 2014; Pandit et al., 2021). They show interaction with both polar and non-polar media. Compared to standard CDs, ACDs offer a broader range of environmental applications. For instance, the amphiphilic fluorescent carbon nanodots detect tetracycline and nitrite in both aqueous and organic media (Omer et al., 2020). Despite the difference in structures, synthetic approaches, precursors, dopants, and chemical functionalities, CDs show similar optical properties (Ozyurt et al., 2023; Das et al., 2021a). They exhibit UV-visible absorbance, which is a convincing parameter in examining the chemical structure of CDs (Das et al., 2021a). CDs show single or more distinguished absorption peaks in the UV region and an extended tail in the visible region (Baker and Baker, 2010; Li D. et al., 2018; Liu, 2020). The 200–280 nm peak is attributed to the π-π^* transition of doubly-bonded carbon atoms, i.e., C=C. The 280–400 nm absorption peak corresponds to the n-π^* transition of C=O. Moreover, the overlapped bands above 400 nm regions correspond to the n-π^* transition, originating from the absorption of surface-states with electron lone-pairs (Liu, 2020; Wang Y. et al., 2014).

However, CDs' photoluminescence (PL) properties are not fully understood (Langer et al., 2021; Zhang et al., 2021; Barman and Patra, 2018; Sk et al., 2014). The two major causes for the uncertain PL mechanism are the (i) complex structure of CDs and (ii) variation in the PL centers (Langer et al., 2021). PL of GQDs and CQDs depends on surface states (such as heteroatom dopants, surface functionalities, surface configurations, surface defects, etc.) and quantum confinement effects (QCE) (Cui et al., 2021; Sk et al., 2014; Ai et al., 2021; Zhu Z. et al., 2019). The QCE can be governed by various factors such as particle size, shape, and solvent involved in the synthesis (Sk et al., 2014; Kim et al., 2012; Qu et al., 2015). All these factors affect the sp^2 conjugation length. More significant conjugation length of sp^2 carbon domains results in a reduced band gap, leading to red emission shift (Pedrueza et al., 2013). Likewise, the large, aromatic ring containing GQDs structures shows redshifts (Sk et al., 2014; Kim et al., 2012; Eda et al., 2010). The utilization of certain solvents (for example, DFM) in the synthesis process of CDs also affects the band gap and PL properties (Qu et al., 2016; Tian et al., 2017; Zhu et al., 2011; Bai et al., 2019). On the other hand, the surface states arise synergistic hybridization between the attached functional groups and carbon backbone (Ding H. et al., 2020). Hence, the hetero-atom doping and surface modifications tune the PL properties of CDs (Yuan et al., 2018; Fan et al., 2014). Integrating functionalities (hydroxyl, carbonyl, carboxylic acid, epoxy and epoxy ether, alcohol, amine, and thiol) forms surface states and defects. These surface states shift emission to longer wavelengths. For instance, using tartaric acid in the reaction mixture of CDs synthesis enhances the degree of oxidation and creates redshift. Figure 4 represents the factors affecting the optical properties of CDs.

Heteroatom dopants (B, F, N, and S) also tune the electronic structure and enhance fluorescence quantum yield (Qu et al., 2015; Yang et al., 2018; Peng et al., 2016; Zuo et al., 2017; Hao et al., 2015; Qin Z. et al., 2019; Feng et al., 2021; Gao D. et al., 2020). This property has notably acquired great attention in monitoring and sensing applications of CDs. Furthermore, the pH (Feng T. et al., 2018; Lei et al., 2019; Chao et al., 2020), reaction temperature (Sun et al., 2020; Chen et al., 2017; Miao et al., 2018), concentration (Chen et al., 2018; Meng et al., 2017; Wang et al., 2018a; Ba et al., 2020; Zhang et al., 2019; Su et al., 2020), and aggregations (Wang et al., 2017; Lv et al., 2019; Chen et al., 2012; Yang et al., 2019) dependent PL properties of CDs have also been reported. Moreover, CDs exhibit good chemical stability. Chiral CDs show more excellent chemical stability than the simple CDs (Li S. et al., 2021; Ru et al., 2020). Compared to metal complexes, metal-doped CDs exhibit a low degree of cytotoxicity. It is because of the presence of carbon, which hinders the free release of metal ions (Li X. et al., 2022).

Furthermore, the study of chemical properties involves the consideration of CDs structure. Several characterization techniques are employed (Ozyurt et al., 2023; Song et al., 2015; Bhaisare et al., 2015; Singh et al., 2018; Siddique et al., 2018). These techniques include scrutinizing size, shape, crystal structure, chemical functionality, and particle-size distribution (Ozyurt et al., 2023). Regarding the size, shape, and average-size investigation, TEM (Transmission Electron Microscopy) is preferably a significant analytical technique (Song et al., 2015; Bhaisare et al., 2015; Singh et al., 2018). TEM images also reveal the functional groups present on GQDs. Whereas, determining particle-thickness involves using AFM (Atomic Force Microscopy). It also gives information about topological profile and graphene-layer count in GQDs (Ozyurt et al., 2023). However, the crystal structure can be

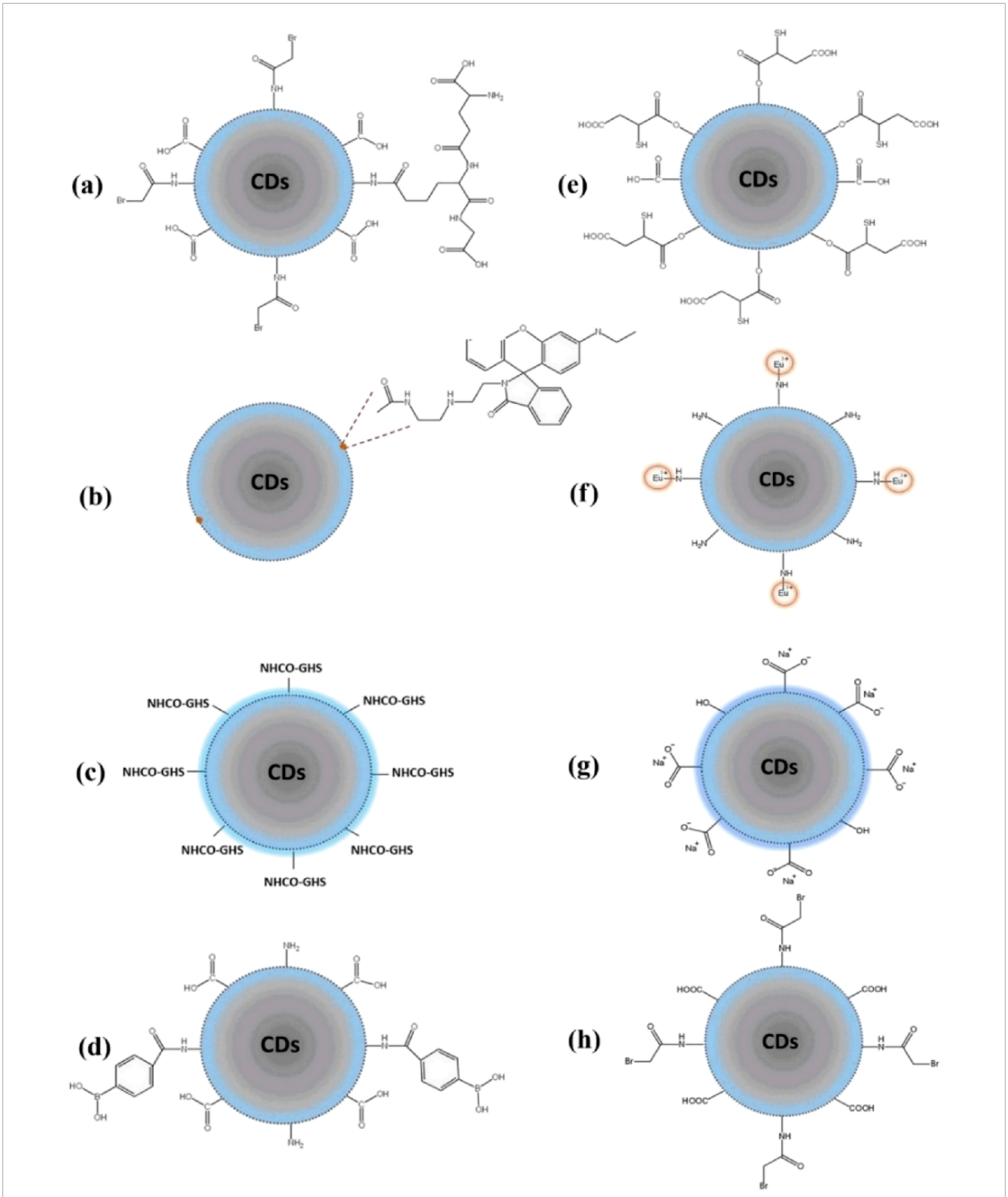


FIGURE 3
Illustration of Structural Functionalities Present on Carbon Dots developed via Amide Coupling Reaction in **(a–d, h)**; Esterification Reaction in **(e)**; Sulfonylation Reaction in **(f)** and Complexation in **(g)**.

investigated by HRTEM (High-Resolution Transmission Electron Microscopy and XRD (X-ray Diffraction) (Mintz et al., 2021; Nie et al., 2014). HRTEM images represent the crystallographic planes, i.e., lattice fringes in CD-aggregates (Nie et al., 2014; Kurdekar et al., 2016). Raman Spectroscopy is used to investigate CDs' crystallinity and functional groups (Dager et al., 2019).

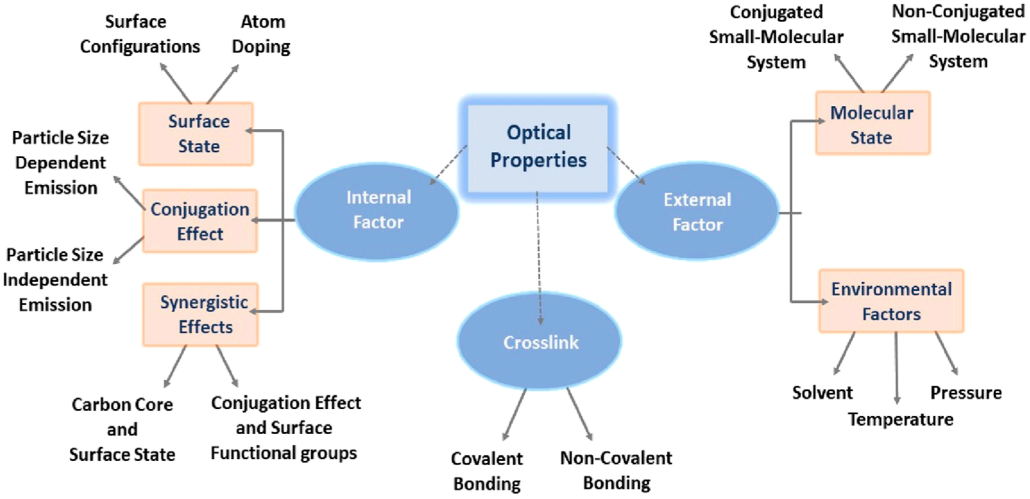


FIGURE 4
Factors affecting optical properties of carbon dots (CDs).

In Raman spectra, CDs show two bands, i.e., G and D bands (Ozyurt et al., 2023). The D and G band correspond to the vibration originating from graphitic sp^3-carbon and graphitic sp^2-carbon defects (edges) (Shi et al., 2015). The surface functional group on CDs can be recognized through Elementary Analysis and Infrared Spectroscopy (El-Shafey, 2021). The chemical functionalities can be identified by X-ray Photoelectron Spectroscopy, Nuclear Resonance Spectroscopy (NMR), and Fourier transform infrared (FTIR) technique (Ozyurt et al., 2023).

4 Metal-based functionalization of CDs

Due to the easy preparation and potent applications, CDs' functionalization has attracted researchers' attention (Đorđević et al., 2019; Stepanidenko et al., 2021; Park et al., 2016). Functionalization controls and enhances CDs' optical, electrical, chemical, and biological properties (Li X. et al., 2022; Park et al., 2016; Chen et al., 2019; Dhenadhayalan et al., 2020). Surface modification and doping are the two major approaches for CDs functionalization. In surface modification, functional ligands such as ions, polymers, proteins, DNA, or other molecules modify CDs. The CD-surface and functional ligand interact through electrostatic interaction, covalent bond, non-covalent bond, or coordination (Chen et al., 2019). Along with the improvement in properties, surface modification provides new reaction sites for more surface reactions to occur as well (Wang et al., 2023). Fe^{3+}, Mn^{2+}, Cu^{2+}, Tb^{3+}, and Eu^{3+} have been utilized in the surface modification of CDs (Bourlinos et al., 2017; Wang Y. et al., 2015).

Doping also optimizes the physicochemical properties of CDs. It causes variation in the intrinsic structure of CDs, and eventually, the electronic distribution changes through the generation of n-type or *p*-type carriers (Li X. et al., 2022; Chen et al., 2019). The introduction of copper-metal causes an enhancement in the electronic properties, which improves the catalytic properties of CDs (Duan et al., 2019). Doping can be further classified into metal doping or non-metal doping. Boron, nitrogen, phosphorus, sulfur, and fluorine (either solely or in combination) are non-metallic dopants. Calcium, magnesium, scandium, manganese, iron, copper, nickel, cobalt, zinc, gallium, bismuth, molybdenum, silver, gold, gadolinium, etc., act as metallic dopants. Both metallic and non-metallic dopants design HOMO-LUMO energy band gaps. This energy band gap decides doped CDs' (photo-optical) properties (Kumar et al., 2022; Feng J. et al., 2018).

Due to more electrons, unoccupied orbitals, and large atomic radii of metal ions, metal-based CDs offer a broad range of intrinsic properties. Research shows that Cu-based doping can increase the electron-donating and accepting abilities, resulting in copper-to-graphite charge transfer, and eventually, the electrical conductivity is enhanced (Wu et al., 2015). Another research shows that the Cu-doped CQDs can form Cu-N bonding, which produces the copper-to-graphite charge transfer. Ultimately, the absorption intensity increases (Eda et al., 2010; Wu et al., 2015). Owing to the low energy level, when UV light of 365 nm strikes the Cu-doped CQDs, the photo-excited holes intensely compete with Cu ions, which results in the production of Cu ions, enabling their utilization for Husigen 1,3 dipolar cyclo-addition reaction (Li et al., 2015). Figure 5b represents the Cu^{2+}-based synthesis of CDs (Jin et al., 2017). These functionalized CDs are synthesized by using carrots as a carbon source. The CDs were modified using positively charged polyethylene (PEI) and Nile Blue. The significance of these functionalized CDs lies in their action as a two-photon fluorescence probe. Mn-based functionalization of CDs can adjust the fluorescent emission, resulting in emission at longer wavelength (Chen et al., 2019). In addition, zinc doping has been proposed to give higher photocatalytic activity and QY (Chen et al., 2019; Li et al., 2013; Xu et al., 2016). Moreover, Zn-doped CDs pose stabilized excited states, increasing the fluorescence lifetime. The defects present in Zn-CDs enhance solubility and are helpful for the photodegradation of Cr(VI) (Chen et al., 2019). It has been reported

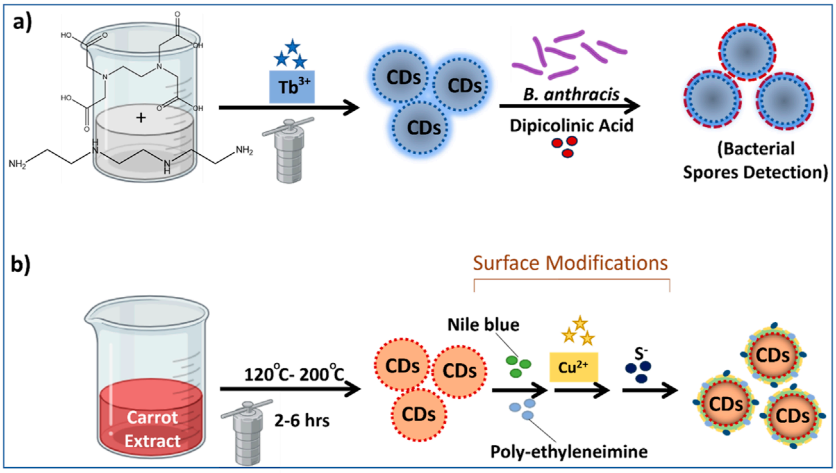


FIGURE 5
Surface functionalization of carbon dots (CDs), **(a)** Terbium-based CDs, and **(b)** Copper-based CDs.

that CDs with transition metal ions exhibit higher efficiency than non-transition ones (Bandi et al., 2022).

Lanthanides-based functionalized CDs have gained much importance due to their unique fluorescent properties (Chen et al., 2019). Gd, Y, Nd, Tb, Tm, and Eu have been utilized to functionalize metal-doped CDs (Chen B. B. et al., 2016; Chen Y. et al., 2016). However, Y and Nd are highly significant for their long fluorescence lifetime NIR emission. Nd $^{3+}$ and Yb^{3+} have been utilized as dopants to synthesize Ln-based CQDs exhibiting characteristic NIR emission (Wu et al., 2016). In addition, Eu-based CDs have also been prepared via a microwave-assisted method. Eu functionalized CDs offer exceptionally enhanced quantum yield (QY) (Chen Y. et al., 2016). Figure 5a represents the Tb^{3+}-based functionalization of CDs (Chen et al., 2015). The Tb^{3+}-based CDs were synthesized by complexing Terbium with amino and carboxyl groups on the CD surface. These functionalized CDs can detect dipicolinic acid. Regarding their application, they can rapidly detect biomolecules and bacterial spores.

Another common approach for the metal-based functionalization of CDs involves using noble metals (Ru, Rh, Os, Ir, Pt, Au, and Ag) as dopants (Zaheer et al., 2023). Noble metal-based CDs contain a synergistic effect of both components, i.e., noble metal and CDs (Fu et al., 2020). Functionalization usually occurs through ion exchange, hydrothermal, or galvanic replacement reactions (GRR). These functionalized CDs pose advanced properties, such as a specific large surface area, extensive catalytic activity, and sufficient electron transfer pathways (Zaheer et al., 2023).

Metal-based functionalization of CDs pursues vast applications in the degradation and adsorption of pollutants from the environment (Gallareta-Olivares et al., 2023). Cu, Fe, Ga, Zn, Au, and Ag are excellent metal dopants in catalysis. Due to copper atoms (which act as both electron donor and acceptor), Co-based CDs are considered a strong catalyst (Ma et al., 2017). Fe, Zn, and Cr can be doped into CDs for metal detection in water (Han et al., 2018; Xu et al., 2018; Zhang H.-Y. et al., 2017). Fe^{2+} doped CDs were synthesized for enhanced fluorescence and detection specificity (Han et al., 2018). Cu-CDs catalyze the ozonation reaction of textile dyes, i.e., Methyl Orange (MO), Reactive Black 5 (RB-5), Orange II sodium salt (Orange (II)), and Remazol Brilliant Blue R (RBB-R). In the absence of Cu-CDs, the rate of discoloration is low. The presence of Cu-CDs results in increases in the rate of reaction (%Inc = 24%) with 90% efficiency in 60 min for azo dyes (i.e., MO, O (II) and RB-R) and 30 min for anthraquinone dye (i.e., RBB-5). However, the presence of carbonate in water inhibits the ozone decomposition. Hence, the high concentration of carbonates in textile sewers limits the application of Cu-CDs for wastewater treatment.

Moreover, studies show that Zn^{2+} improves the fluorescence of silver nanoclusters (Xu et al., 2018). Zn-CDs and Co-CDs can be utilized to detect Hg^{2+} and Cr (IV) ions in water, respectively (Xu et al., 2018; Zhang H.-Y. et al., 2017). Cu and Ni can be used for CDs' doping in NIR-mediated phototherapy. Thiophanate-methyl (TM) is a potent fungicide that can be detected and treated in Cu-based CDs (Han et al., 2019). This sensor overcomes the single response drawback of ratiometric fluorescent sensors. Cr (III)-based CDs were effectively demonstrated to detect *p*-nitrophenol, which acts as a pesticide (Li C. et al., 2019). Moreover, Mg-based N-CDs (formed via co-doping) act as a paraoxon-insecticide detector (Peng et al., 2019). Zn/ZnO-based nanocomposites, BiOCl hybrid nanocomposites, and Cu, N co-doped CDs were also reported to perform photodegradation of pollutants (Guo et al., 2017; Phophayu et al., 2020; Mou et al., 2019; Mu et al., 2019). Subsequently, Bi-based CDs can remove dyes and metal contaminants from water. Several other environmentally related applications of CDs/functionalized CDs and metal doped and Hybrid CDs are summarized in Table 1.

5 Solvothermal vs. hydrothermal synthesis route

The development of solvothermal and hydrothermal synthesis routes has more than 100 years of history. Both methods are inexpensive, rapid, effective, and environmentally friendly

(Li X. et al., 2022; Feng and Li, 2017; Tejwan et al., 2021; Ndlwana et al., 2021). These routes are significant for the current and future fabrication and tuning of CDs for several applications in catalysis, water treatment, pollutant degradation, metal detection, and the biomedical field (Wang et al., 2018b; Manohara et al., 2019; Zhou et al., 2021; Ge et al., 2021). The synthesis involves heating precursor solutions at a high temperature for many hours (Li X. et al., 2022). Usually, metallic salts and organic molecules are utilized as precursors. The prepared particles exhibit a diameter of less than 10 nm. Solvothermal and hydrothermal methods are similar to each other. However, in the solvothermal method, the organic solvent is used instead of water (Li X. et al., 2022; Tejwan et al., 2021). Research reports that Mn, Cu, Zn, Mg, Gd, Co, Ag, and Cr ions have been doped on CDs through solvothermal synthesis (Li X. et al., 2022).

Wang et al. prepared porous carbon-protected magnetite (Fe_3O_4@C) nanoparticles from ferrocene ($Fe(C_5H_5)_2$) and hydrogen peroxide (H_2O_2) using acetone (Wang H. et al., 2013). This solvothermal synthesis was accomplished at 200°C in 24 h. Later, Fe_3O_4@C nanoparticles were loaded with silver ions (Ag^+), followed by the *in situ* Ag^+ reduction in the carbon shell at room temperature. Dumbbell-shaped Fe_3O_4@C-Ag hybrid nanoparticles were synthesized, having 110 nm size. These catalytic hybrid nanoparticles enhanced the reduction reaction of organic dyes in water. Due to the carbon shell protection, these nanoparticles also resisted photo-bleaching.

Using solvothermal treatment, Zhang et al. synthesized Co-doped CDs (CCDs) from 1-(2-Pyridylazo)-2-naphthol, $CoCl_2$, and ethanol as solvent. Based on photoluminescence quenching, these CCDs were successfully utilized to sense Cr(VI) in water. The author proposed that the fluorescence of CCDs could be quenched in the presence of Cr(VI) ions. The detection limit calculated was 0.12 ppm for Cr(VI). These CCDs help control chromium contaminant intake from water and reservoirs. Wang et al. synthesized spherical, 100 nm-sized hybrid-nanoparticles of iron oxide-fluorescent CDs from a solvothermal route in which acetone solvent was used (Wang H. et al., 2014). The reaction was held in an autoclave for 48 h at 200°C, followed by 15 min of sonication at room temperature. These hybrid nanoparticles exhibited NIR light-absorbing properties, upconversion fluorescent activity, and high magnetic response.

Zhou et al. used citric acid, urea, $Mn(OAc)_2$, and toluene as solvents to synthesize Mn-based CDs (2.95 nm diameter) (Liu Y. et al., 2018). In these CDs, the release of Mn^{2+} enhanced the degree of conjugated sp^2 domain, surface states, and FLQY up to 68.6%. A synergistic strategy was observed to develop these efficient CDs, in which solvent worked as a tuning agent and Mn^{2+} as an enhancing agent. The author demonstrated that the solvent is a primary factor in tailoring the absorption band. These Mn-based CDs exhibit versatile properties to peruse several applications.

Wang et al. fabricated magnetite-porous carbon-protected Au-based nanoparticles (AuNPs) through a solvothermal technique (Wang H. et al., 2015). They utilized Fe_3O_4@PC-CDs and Fe_3O_4@PC-CDs-Ag and then proceeded with a galvanic cell reaction to replace Ag with Au^{3+} in the presence of $HAuCl_4$. The product achieved was Fe_3O_4@PC-CDs-Au nanoparticles. These Au-doped hybrid nanoparticles show high photothermal conversion and enhance photo-stability. Liu et al. prepared NiFe2O4 integrated EDTA-derived CDs from a solvothermal route, in which $NiCl_2$, $FeCl_3.6H_2O$, and NaAc were dissolved in ethylene glycol (Liu et al., 2017). After the sonication, the reaction mixture was autoclaved for 10 h at 200°C. These Ni/Fe-based CDs exhibit high water dispersibility and excellent adsorption of tetracycline from water. Using a hydrothermal approach, Sachdev et al. prepared multifunctional CeO_2-based spherical CDs (Sachdev and Gopinath, 2016). The reaction of ammonium cerium branched poly (ethyleneimine), and aqueous solution form of chitosan proceeded at 220°C for 12 h. The author demonstrated that, due to the catalytic effect of CeO_2, these nanocomposites can interact and neutralize hydrogen peroxide. Thus, they prevent the fluorescent activity of CDs.

Yang et al. fabricated Mg/N co-doped CDs by hydrothermal method at 200°C and 5 h (Yang et al., 2016). They utilized acrylic acid, magnesium hydroxide, and ethylenediamine, followed by the conjugation of CDs with Cholrin e6. These CDs show a QY of 84.6%, along with high fluorescence resonance energy transfer (FRET). The CDs-Ce6 system offers high hydrophobicity and changeable FRET efficiency as well. Zhang et al. synthesized La-doped CQDs (La-CQDs) from hydrothermal treatment at 160°C for 8 h (Zhang et al., 2017b). They used ATP and $LaCl_3.2H_2O$ to form La-CQDs (4.3 ± 0.3 nm diameter). These CQDs show high thermal stability and intense fluorescence. Due to numerous -COOH, $-NH_2$, PO_4^{3-} and -OH groups, La-LQDs have excellent photoluminescence and high-water solubility. These CQDs have significantly detected Hg^{2+} (detection limit observed = 0.1 μM).

Zhang et al. synthesized intrinsic photoluminescent and magneto-fluorescent Fe/N co-doped spherical CDs (FeN@CDs) by facile hydrothermal method at 200°C for 10 h (Zhang et al., 2017c). Initially, they utilized $FeCl_3.6H_2O$ and chitosan to prepare FeN@CDs. These FeN@CDs were further conjugated with riboflavin and folic acid. The T2 relaxation time increased with the increase in iron concentration. Later, their cross-linked polymer nanostructures were utilized to achieve NIR-triggered photothermal and photodynamic therapy. Das et al. (2018) synthesized spherical N/Zn co-doped CDs (4.5 nm diameter) via hydrothermal treatment at 200°C for 4 h using citric acid, zinc acetate, and tris(hydroxymethyl)aminomethane (Das et al., 2018). These CDs exhibited high fluorescence, QY, monodispersity, and thermal stability. Due to their excellent luminescence, N/Zn co-doped CDs also act as an intriguing FL-probe for detecting H_2O_2 in the Fenton reaction mechanism.

Moradlou et al. synthesized CQDs of hematite nanostructure deposited on titanium (CQDs@α -Fe_2O_3) via hydrothermal treatment of Fe^{3+}, CQDs, $NaNO_3$ and Ti sheet for 6 h at 100°C temperature (Moradlou et al., 2019). Qing et al. fabricated low-cost Cu^{2+-}based CDs using a one-step hydrothermal carbonization treatment of waste tea extract, copper acetate, and ethylenediamine at 150°C temperature for 6 h (Qing et al., 2020). Malmir et al. opted for a hydrothermal technique to synthesize TiO_2-based CQs nanocomposites (Malmir et al., 2020). They used chitosan, ascorbic acid, and TiO_2 at 140 °C for 24 h.

Water is safe, non-toxic, cheap, green, and readily available solvent. In contrast, most organic solvents are expensive, toxic, and hazardous to living and non-living systems. Organic solvents can also change the concentration of reactive species in the reaction

mixture, which ultimately changes the product composition (Feng and Li, 2017). Thus, hydrothermal is a more significant and popular technique for preparing metal-based CDs. Table 2 summarizes various hydrothermally synthesized metal doped and hybrid CDs involved in environmental remediation.

6 CDs as promising enzyme mimics

It is practically significant to synthesize enzyme-mimicking nanomaterial to tackle the intrinsic limitations of natural enzymes (Dhiman et al., 2022; Jin et al., 2021). Nanozymes effectively mimic the catalytic sites of natural enzymes (Li Y. et al., 2020). Representative examples of enzyme mimetic metal-doped and hybrid CDs are summarized in Table 3. They show numerous properties, such as facile synthesis, high catalytic stability, easy modification, and long storage time (Jin et al., 2021; Sun et al., 2018; Huang et al., 2019). They can be remotely controlled with stimuli such as heat, light, ultrasound, and magnetic field (Jiang et al., 2019). The three different possibilities in which CDs exhibit enzyme-like properties are heteroatom-doped CDs, CD-based nanozyme hybrids, and pristine CDs with innate enzyme-mimic properties (Lopez-Cantu et al., 2022). Researchers have studied the enzyme-mimicking properties in pristine CDs (Zhu et al., 2014; Das et al., 2021b). In pristine CDs, oxidase-like activity is based on the adsorption of dissolved oxygen. This adsorption is followed by the transfer of delocalized electrons (of CDs (Li S. et al., 2020)) to oxygen. Ultimately, the oxygen reduces into O^{2-} (Li S. et al., 2020; Li F. et al., 2020). However, nanozymes based on pristine CDs give decreased catalytic activity in neutral pH conditions. Hence, the researchers proposed the CD-based hybrid nanozymes. CuZn-based CDs show catalase-like activity (Xue et al., 2021). The CDs were covalently doped with copper and zinc. These CDs exhibit high stability and excellent electron transfer capability. Zhuo et al. synthesized oxidase-like Mn-doped CDs (Mn-CDs) via facile hydrothermal method. These CDs catalyzed the oxidation of 3,3′,5,5,-tetramethylbenzidine. Su et al. fabricated Co/N-doped CDs using $Co(NH_3)_2.6H_2O$ and Nitrogen-CDs. These CDs exhibited peroxidase-lie catalytic activity to *o*-phenyldiamine (Su et al., 2022). Yang et al. synthesized Iron and nitrogen co-doped CDs via a facile solvothermal method (Figure 6a; Yang et al., 2017). These CDs exhibit high water solubility and dimensional homogeneity. The intrinsic peroxidase-like (POD-like) activity of N, Fe-CDs is attributed to iron-doping. In the presence of H_2O_2 N, Fe-CDs catalyze the oxidation of TMB and form blue-colored TMBox as an oxidation product. Hence, they act as highly efficient peroxidase mimetic and promising probes in chemical and biological reactions. Likewise, the Copper and Chlorine (Cu, Cl-CDs co-doped CDs were synthesized via a hydrothermal method (Zhao et al., 2022). N, Cu-CDs exhibit both oxidase- and peroxidase-like activity. Figure 6b represents the synthesis, oxidase-like (OD-like), and peroxidase-like (POD-like) activity of N, Cu-CDs. The limit of detection for TMB and hydroquinone (HQ) is 0.35 μM and 0.08 μM, respectively.

Duan et al. synthesized Cu-doped CDs using a solid-phase synthesis technique using $Cu(NO_3)_2.3H_2O$ dopant (Duan et al., 2019). These CDs exhibited catalytic properties and specifically showed peroxidase-like activity. Moreover, Cu-CDs show good stability and enzyme-like activity in a broad range of temperature and pH values. Several oxidase-like enzymes have been synthesized with a relevant interest. These metal-doped CDs can catalyze oxidation reactions in the presence of dioxygen (Lopez-Cantu et al., 2022). Dioxygen accepts electrons and gives the formation of water and hydrogen peroxide. Li et al. synthesized cerium-mediated CD-based nanozyme, exhibiting oxidase-like activity (Li S. et al., 2020). Its catalytic activity could be tailored by changing the concentration ratio of CDs and Cerium ions. Researchers have also synthesized CD-based nanozyme hybrids with other materials. This approach develops a synergistic effect to increase the enzymatic properties of CDs (Ngo et al., 2021). Metal-doped carbon-based nanozymes work as electron transport mediators; thus, the reaction rate increases (Feng et al., 2022). The synergism between metal and carbon structures increases the electron flow in enzymatic processes. Subsequently, these nanozymes provide a large surface area and hinder metal agglomeration (Sun Y. et al., 2023).

Zhuo et al. synthesized dSCSAu-NCDs hybrid nanostructures (Zhao L. et al., 2020) (Figure 6c). The CDs were immobilized into amino-based dendritic silica spheres (dSs) with linked gold nanoclusters (Au-NCs). This hybrid nanostructure based on dual-nanozymes shows superoxide dismutase-like activity. The single-atom strategy is another significant approach to tuning the electronic and catalytic properties (Wu et al., 2020). This strategy overcomes the conventional doping limitations and provides excellent dispersibility and utilization of functionalized CDs (Sun Y. et al., 2023). Researchers have reported several single-atom nanozymes. For instance, Qin et al. synthesized PEGylated silica-based Fe single-atom CDs (Fe/CDs@PPSNs). These nanostructures exhibited higher catalytic activity than simple iron oxide-based CDs (Qin et al., 2022). Single-atom Ru-based CDs have been synthesized to achieve catalytic activities (Wang W. et al., 2021). These CDs exhibit peroxidase, oxidase, and glutathione oxidase-like activity. Theoretical results show that these CDs more specifically mimic peroxidase-like activity. The Ru-4d orbital electrons are transferred to the oxygen atom of hydrogen peroxide. It results in the production of hydro-oxide radicals.

7 CDs as nanozymes with peroxidase-like catalytic activities

Natural peroxidases belong to a large group of oxidoreductases, which functionally catalyze the reduction of peroxides and oxidation of inorganic and organic compounds (Hamid and Khalil-ur-Rehman, 2009; de Oliveira et al., 2021). Chemically, these comprise heam proteins containing Fe (III) with protoporphyrin IX as a prosthetic group. NADH, glutathione, and iodine peroxidase are specific enzymes belonging to the peroxidase group (Li M. et al., 2023; Shigeto and Tsutsumi, 2016; Riyazuddin et al., 2023). However, the non-specific enzymes are referred to as peroxidases. Peroxidase catalytic activity is essential in the chemical, environmental, biomedical, and industrial fields (Jiang et al., 2019; Passardi et al., 2005; Neill et al., 2002). The immobilized oxidative enzymes are widely significant and suitable to tackle the current challenges of environmental pollution (Wei et al., 2020; Aitken et al., 1994; Dasappa and Loehr, 1991).

Regarding the peroxidase-like catalytic phenomenon of CDs, many authors reported the occurrence of a "Ping-Pong catalytic

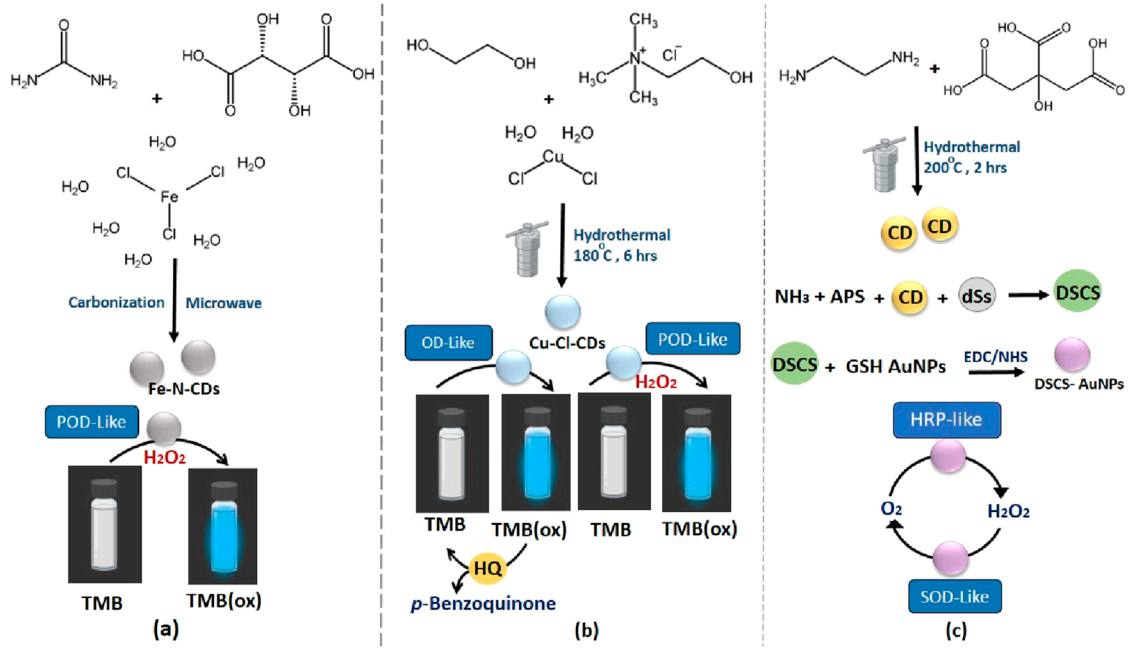


FIGURE 6
Functionalized CDs illustrating enzyme-like capacities, **(a)** peroxidase-like (POD-like) activity, **(b)** oxidase-like (OD-like) activity and peroxidase-like (POD-like) activity, and **(c)** superoxide dismutase (SOD-like) activity and horseradish peroxidase-like (HRP-like) activity.

mechanism" (Shi et al., 2011; Wang B. et al., 2016; Shamsipur et al., 2014; Mohammadpour et al., 2014; Long et al., 2016; Zhu et al., 2015). However, depending on the nanozyme composition, the action mechanism may vary. On the other hand, two substrates, i.e., a hydrogen acceptor and a hydrogen donor, are generally involved in the catalytic reaction. The nanozymes reduce the H_2O_2 and generate reactive intermediates such as ·OH. ·OH further reacts with the second substrate to proceed with the reaction (Gao L. et al., 2020). In another research, a systematic study reports that the catalytic activity can be induced by the presence of hydrophilic groups (such as -COOH, -C=O, and -NH_2) on the CD surface (Das et al., 2021b). These groups generate an affinity with peroxides, ultimately acting as a catalytic site for catalyzed reactions. The author reported that the carboxylic group induces maximum peroxidase-like activity in CDs. Nitrogen and copper co-doped CDs (N, Cu-CDs) were synthesized via a facile hydrothermal method (Lin et al., 2019). These CDs exhibit peroxidase-like (POD) catalytic activity even at a broader range of pH and temperature. The POD-like activity of N, Cu-CDs catalyzes the oxidation of para-, ortho-, and *m*-phenylenediamine by peroxide. The oxidation products of *o*-phenylenediamine (OPD) and *p*-phenylenediamine are yellow and brown, respectively. Hence, the POD-like N, Cu-CDs result in the colorimetric discrimination of OPD and PPD.

The extent of peroxidase-like activity of metal-doped CDs depends on different factors, such as the electron transferring capacity and variable valance states of dopant-metal (Li S. et al., 2018; Berglund et al., 2002). The significance of the electron transfer process in enhancing the peroxidase-like activity of CDs has been reported (Shamsipur et al., 2014). For instance, CDs with greater charge density show enhanced electron transfer from substrate to CDs. The substrate oxidation reaction rate increases due to enhanced electron transfer and radical formation. Moreover, CDs with smaller sizes and larger specific surfaces exhibit more excellent peroxidase-like catalytic activity (Zhou et al., 2019; Tang et al., 2019). Figure 7a represents the hydrothermal synthesis of peroxidase-like Fe-CDs (Zhu D. et al., 2019). Methylthymol blue sodium and ferric chloride hexahydrate were used as carbon and metal precursor/sources, respectively. The catalytic activity of Fe-CDs corresponds to the oxidation of the colorless o-phenylenediamine (OPD) solution. Under the peroxidase-like activity of Fe-CDs, the oxidation product OPD forms 2,3-diaminophenazine (DAP). The sensing of H_2O_2 (detection limit 0.47 μM) is based on the visible yellow color formed in Fe-CDs/H_2O_2/OPD (Figure 7b).

Pristine, doped, and/or hybrid CD nanozymes have been reported to exhibit peroxidase-like activity (Figure 8; Zhu et al., 2014; Duan et al., 2019; Li Y. et al., 2020; Shamsipur et al., 2014; Tang et al., 2019; Zhang L. et al., 2017; Wu et al., 2014; Zheng et al., 2016; Dong et al., 2015; Gan et al., 2021; Yang et al., 2021; Habibi and Heidari, 2016; Roushani et al., 2018). In this manner, Figure 8 represents the CDs, Co@CDs, Gd-CDs, and N, Cu-CDs as pristine, hybrid, doped, and co-doped CDs with peroxidase-like activities.

Along with catalytic activity, few nanozymes show highly unique properties. Wang et al. synthesized multicolor photoluminescent CNPs ($C_1H_{0.677}O_{0.586}N_{0.015}Na_{0.069}$) with high catalytic activity (Wang et al., 2011). The EDX spectrum of these CNPs demonstrated that no metal catalyst was involved in the system. Na^+ only acts as a counter ion and exhibits no catalytic activity. Similarly, CNPs and peroxide could not oxidize the substrate. However, there existed an interaction between CNPs, peroxide and substrate. This interaction induces catalytic activity in CNPs. Several Hybrid

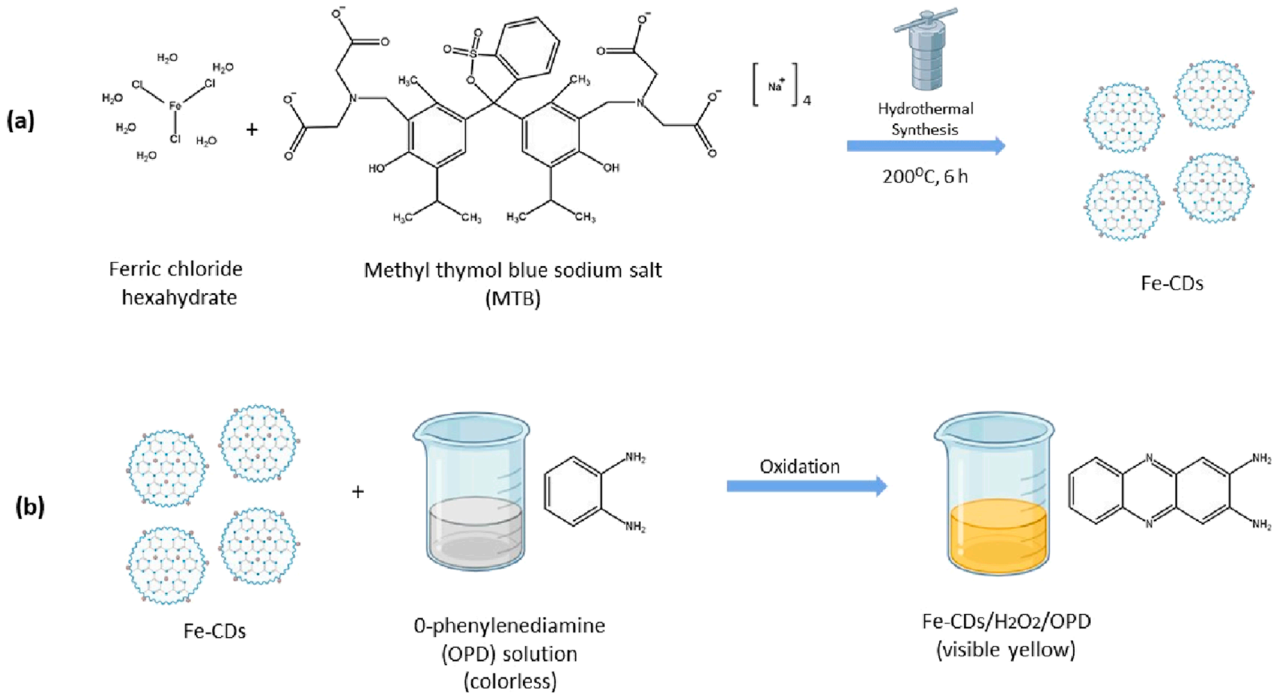


FIGURE 7
(a) Synthesis of peroxidase-like Fe-CDs **(b)** Fluorescent sensing of H_2O_2 in the presence of Fe-CDs.

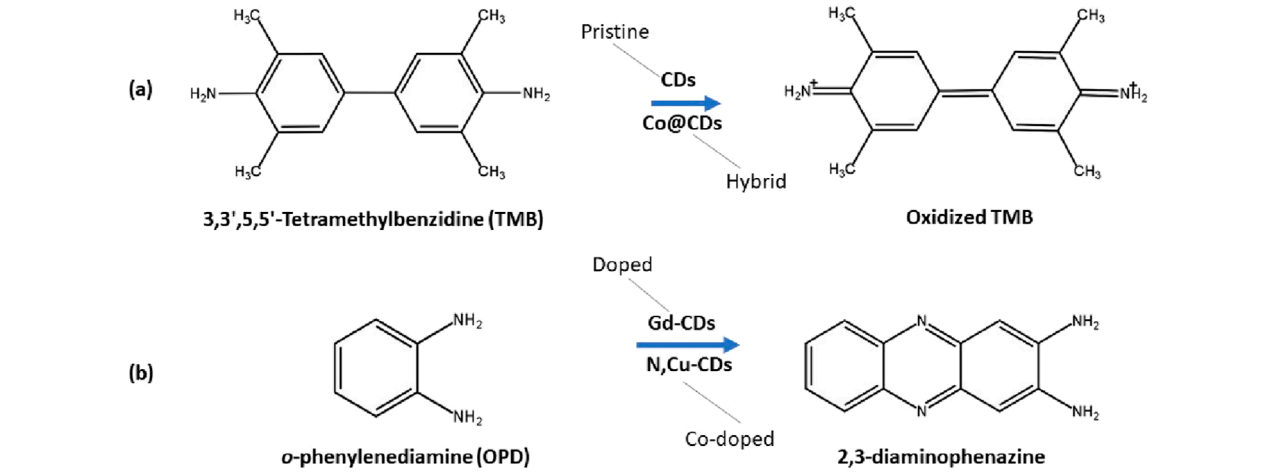


FIGURE 8
(a) Catalytic Oxidation of 3,3′5,5′-Tetramethylbenzidine (TMB) in the presence of CDs and Co@CDs, and **(b)** o-Phenylenediamine in the presence of Gd-CDs and N,Cu-CDs.

nanozymes with excellent temperature and pH tolerability (such as thermally stable Fe_3O_4/GQD-based nanozymes, thermally stable and reusable NCDs/Fe_3O_4-based nanozymes and acid pH-independent Co, N-doped CD-based hybrid nanozymes) have also been reported (Su et al., 2022; Huang et al., 2023; Shen et al., 2019). Likewise, the Cu-doped CDs were synthesized through a facile solid phase treatment of citric acid as a carbon source and $Cu(NO_3)_2.3H_2O$ as a metal source (Duan et al., 2019). These CDs show high stability and excellent peroxidase-like activity within a broad range of pH and temperature. In another research, N, Fe-codoped CDs were synthesized using $FeCl_3.6H_2O$, B-cyclodextrin, and ethylenediamine via hydrothermal treatment at 180°C for half an hour (Li Y. et al., 2020). In the presence of peroxide, these CDs were reported to exhibit color-changing properties along with more excellent catalytic activity than that of horseradish peroxidase (HRP). However, synthesizing peroxidase-like complex CD-based hybrid nanozymes is a relatively complicated but potent approach (Shi et al., 2019). For example, Li et al.

synthesized Au@HgNPs nanozymes using gold nanoparticles (Au-NPs), nor-adrenaline-based CDs (NA-CDs), and methyl mercury ions ($MeHg^+$) (Li Q. et al., 2023). The synthesis phenomenon was observed to be quite complex. However, the radical formation and enhanced electron transfer from metals (Au and Hg) to CDs induce high peroxidase-like catalytic activity in the nanozymes.

8 Environmental application

CD-based nanozymes can be noticeably used to monitor, degrade and adsorb the environmental pollutants (Gallareta-Olivares et al., 2023; Jelinek, 2017; Lin et al., 2018; Liang et al., 2020). Environmental applications of enzyme mimetic metal doped/hybrid CDs are summarized in Table 4. CD-based sensors either directly interact with the analyte and show a change in fluorescence or are functionalized with recognition molecule(s), which detect(s) the target species (Long et al., 2021). In these sensing systems, primarily nanozymes oxidize the peroxide and form $OH^•$. This $OH^•$ proceeds the conversion of substrate into product. These products exhibit different fluorescence, absorbance, and electric properties from those of the substrate. CD-based nanozymes exhibit higher colorimetric and fluorescent detection properties (Long et al., 2021).

Relative to all other analytical methods for sensing environmental pollutants, CD-based fluorescence detection is more efficient, rapid, and straightforward (Sun et al., 2017; Molaei, 2020; Devi et al., 2019). The colorimetric CD-based nanozymes are even more practical, cost-effective, and simpler than fluorescent sensors (Song et al., 2011). Several metal-doped CDs-based nanoparticles, such as CDs@polymoxometallate have been utilized in photocatalytic degradation of organic pollutants (Di et al., 2015). Hydrothermally synthesized, CD-stabilized Cu_4O_3 nanozymes have also been reported to be used in environmental treatments (Li F. et al., 2020). These hybrid nanozymes show a synergistic effect between peroxidase and oxidase-like catalytic activity, leading to the vigorous oxidation of organic dyes. Moreover, CD-stabilized Cu_4O_3 nanocomposites are highly stable, cost-effective, and versatile in photocatalytic applications. Sari et al. also fabricated Fe_3O_4/CDs photocatalysts via hydrothermal technique. These photocatalysts have been demonstrated for dye degradation. Moreover, Fe-N-CDs have been shown to exhibit peroxidase-like activity. Research reveals that the nitrogen doping in CDs (N-CDs) offers pollutant degradation activity. Similarly, Au-nanoparticle loaded graphitic carbon nanosheets offer degradation of organic pollutants. Li et al. synthesized CDs-stabilized Cu_4O_3 (CDs@Cu_4O_3) multi-enzyme mimetics by a hydrothermal method (Li F. et al., 2020). These nanozymes exhibit peroxidase (PD) and oxidase-like (OD) catalytic behavior. Interestingly, the synergistic enhancement effect of PD and OD results in fast oxidation of organic substrates such as methylene blue. Hence, CDs@Cu_4O_3 nanozymes offer wide-ranging uses in environmental treatments.

8.1 Degradation of antibiotics using peroxidase-like CDs

Antibiotics enter the environment in several ways, i.e., synthesis of therapeutic agents, excretion, and discharging of vacant medicines (Larsson, 2014). However, the released concentration of antibiotics through direct disposal from manufacturing sites is higher than that of industrial and excretion effluents. Compared to tetracyclines and fluoroquinolones, penicillin degrades quickly from the environment. The former groups of antibiotics amplify in the surroundings too. Antibiotic residues in water reservoirs eventually cause environmental and organismic health issues. Consequently, deleting antibiotic residues from the environment is necessary (Liu et al., 2024). The competence of CDs to induce peroxidase-like activity significantly enhances the degradation of antibiotics, leading to effective and advanced removal of such polluting agents from various environmental matrices. However, assessing the environmental and safety impacts of metal-doped CDs-based nanozymes is also significant. The presence of heme-consisting peroxidase in organisms utilizes hydrogen peroxide to catalyze the oxidation of various antibiotics. Likewise, the metalloenzymes play a significant role in the degradation of antibiotics. Hence, it is evident that peroxidase-like metal-doped CDs exhibit a promising role in the degradation of antibiotics from the environment. Similarly, CDs/g-C_3N_4/ZnO nanocomposites exhibit highly enhanced photocatalytic activities for the degradation of tetracycline (Guo et al., 2017). The presence of CDs in these nanocomposites significantly proceeds with the catalytic degradation mechanism of tetracycline.

Liu et al. fabricated magnetic $NiFe_2O_4$-carbon dots (NiFeC) with excellent renderability and enhanced TC-removing ability (Liu et al., 2017). The one-pot solvothermal method synthesized these nanocomposites using $FeCl_3$ and EDTA-2Na as precursors. The high surface functionalities and saturation magnetization make NiFeC a promising candidate for TC adsorption from wastewater. Correspondingly, CDs-MgAl-LDHs@MnO_2/Fe_3O_4 micromotors exhibited dual functionality, i.e., the detection and degradation of an oxytetracycline antibiotic from water (Liu et al., 2024). This dual functionality is due to enzymic activity and a self-propelled motion for diffusion in an aqueous solution. In the presence of hydrogen peroxide, these metal-containing CDs-based micromotors promote the degradation of oxytetracycline from water.

8.2 Degradation of pesticides using peroxidase-like CDs

Pesticides have many benefits, yet they give rise to severe environmental issues (Mahmood et al., 2016). They contaminate the environment differently, including excessive use, unchecked disposal, and run-off from crops and storage containers, etc., (Zacharia, 2011). However, their fate in environmental compartments may vary. Organophosphorus pesticides, triazine herbicides, and chlorinated insecticides are extensively utilized and seriously threaten the environment and biodiversity (Ma et al., 2023; Zacharia, 2011). In this regard, CDs' peroxidase-like activity facilitates pesticide degradation through oxidative processes (Almaqdi et al., 2019). Utilizing metal-organic frameworks (MOFs) and CDs enhances the degradation potential, biocompatibility, specificity, and selectivity of nanozymes (Guan et al., 2012; Li P. et al., 2021). Fe-CDs@MOF-808 and Fe-CDs/MOF-808 nanoreactors were

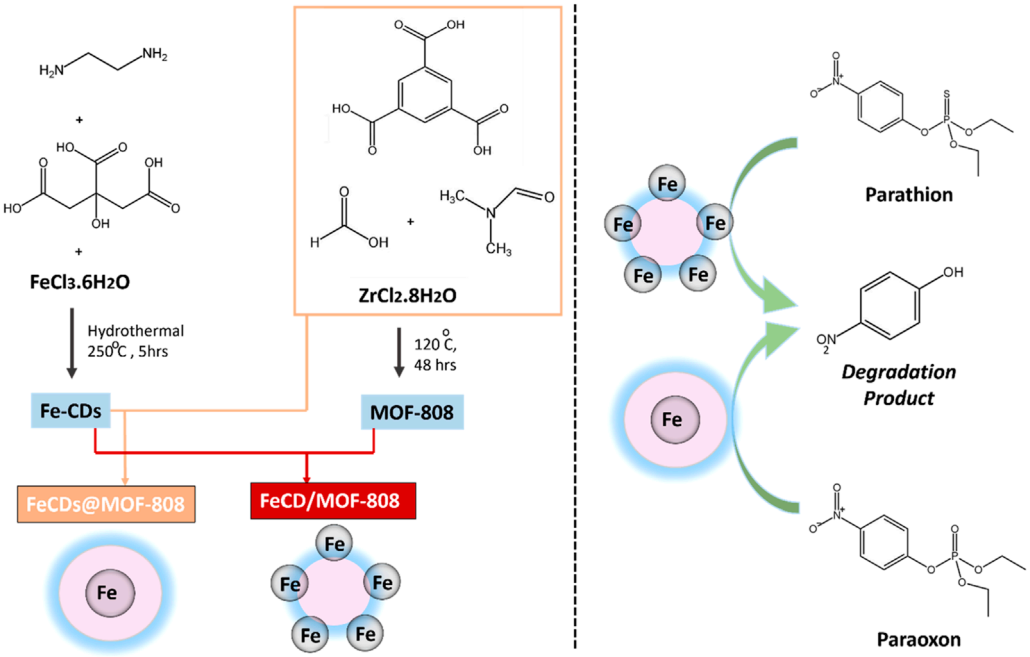


FIGURE 9
Schematic illustration of the synthesis of Fe-CDs@MOF-808 and Fe-CDs/MOF-808 nanoreactors and their deployment for the degradation of pesticides.

synthesized to detect and degrade parathion and paraoxon, respectively (Ma et al., 2023). Fe-CDs detect organophosphorus pesticides and cause the photocatalytic degradation of parathion (Figure 9).

Peroxidase-like nanozymes based on metal-organic frameworks (MOFs) and CDs degrade atrazine (Zhang et al., 2022). Integrating MOFs and CDs results in a highly synergistic system for detecting and degrading atrazine. Depending on the composition of MOF-CD hybrid materials, the peroxidase-like activity could be controllable. Additionally, these nanozymes proceeded with the visual detection and photocatalytic degradation of atrazine in a single process. Furthermore, the heterometallic nanocomposites exhibit higher peroxidase-like activity than single metal or metal oxide-based nanocomposites. For instance, Fe_3O_4-TiO_2/rGO nanocomposites exhibit excellent peroxidase-like activity toward the atrazine degradation (Duarah et al., 2022). In the future, this approach could be suitable for treating triazine herbicides.

8.3 Degradation of phenolics using peroxidase-like CDs

Phenolic compounds are diverse, ranging from simpler phenolic to polymerized compounds (Al Mamari, 2021). Agricultural, industrial, domestic, and natural discharge of these compounds majorly cause environmental pollution (Anku et al., 2017; Fernández et al., 2010). Due to their toxic, carcinogenic, and harmful effects on human health, it is essential to remove phenolic compounds from water (Anku et al., 2017; Rahman et al., 2021; Mu'azu et al., 2017). Carbon-based nanomaterial's significant use and potential as peroxidase-mimetics has been demonstrated for the degradation (removal) of phenolic compounds from water (Zeng et al., 2017). Likewise, metal doping enhances the photocatalytic degradation of phenolic pollutants, too. For example, TiO_2-P25 impregnated with Cr, Cu, and V metals enhances the Vis-light harvesting (Belekbir et al., 2020). Compared to TiO_2-P25, the metal-impregnation in photocatalysts offers more effective removal. However, the mechanisms for enhanced photoactivation may vary for different metals. Correspondingly, the peroxidase-like conjugated system of deuterohemin-peptide and metal-organic framework (DhHP-6-c-ZrMOF) can also degrade phenol. DhHP-6-c-ZrMOF, which acts as a Fenton catalyst, can effectively degrade phenolic pollutants (Ding Y. et al., 2020).

Graphitic carbon nitride/copper-doped CDs nanocomposites (g-C_3N_4/Cu-CDs) offer the potential for the degradation of phenolics from water (Li Q. et al., 2022). They exhibit both oxidase and peroxidase-like catalytic activity. And the graphitic carbon nitride (g-C_3N_4) synergies the nanozymic-activity of Cu-CDs. These nanocomposites also detect phenolic compounds. Introducing H_2O_2 in the g-C_3N_4/Cu-CDs system enhances the oxidation of o-phenylenediamine (OPD) into a fluorescent compound 2,3-diaminophenazine (DAP). This oxidation process gives yellow fluorescence. However, phenolic substances with OPD + H_2O_2+g-C_3N_4/Cu-CDs (combined system) diminish the yellow fluorescence. This phenomenon helps to detect phenolic compounds in water. Moreover, the oxidase-like activity of g-C_3N_4/Cu-CDs converts the phenol and 4-aminoantipyrin into quinoeimine chromogen.

9 Novelties and challenges

Metal-doped and hybrid CDs as enzyme mimics are cutting-edge innovations, offering novelties in environmental remediations and research techniques. For instance, the nucleation of silver-doped and palladium-doped CDs (Ag@CDs and Pd@CDs) is a novel approach to discoloring methylene blue (MB) in daylight. Moreover, the incorporation of metals in CQDs corresponds to synergistic effects in the sensing and catalytic performance. Metal-doped CQDs have also shown the property of boosting electron transfer and photooxidation reactions. Owing to such properties, metal-doped CDs emerge as novel candidates in biomedical and environmental applications.

However, the research is still in its early stages. CDs lack systematic and ascendable synthesis methodology for developing cost-effective and reproducible applications compared to carbon nanomaterials. The effect of CD structures (such as size, morphology, presence of functional groups, and surface states), precursors, impurities, and reaction conditions (such as pH, time, and temperature) on the final product's performance must be examined systematically. Owing to the non-standard synthetic routes, the exact formation process and nucleation mechanisms are also undefined. Moreover, the intrinsic mechanism of PL emission in CDs is unclear (Ai et al., 2021). It is also unclear how metal dopants enhance the fluorescence properties of carbon dots. To determine the PL mechanism to a greater extent, more research work (based on advanced structural characterization techniques such as spherical-aberration correction electron microscopy, synchronous X-ray radiation, and matrix-assisted laser desorption ionization time-of-flight mass spectroscopy, and theoretical examination) is required (Liu J. et al., 2020).

Similarly, metal doping on the CD's center or edge remains challenging. Metal-doped CDs also lack proper characterization techniques to identify whether the dopants are integrated into the carbonaceous core's lattice or CD's surface. Metal ions exhibit redox properties, adversely affecting metal-doped CDs' synthesis process. These ions may form metal oxides required to isolate from M-CDs. Incorporating metal ions in the carbon dots also introduces negative concerns, such as metal toxicity, synthesis complexity, limited stability, and increased cost considerations. Each system of nanozyme possesses a different performance, which can only be explained by a specific mechanism. Hence, further research is needed to understand the structure-activity relation thoroughly. Moreover, the environmental applications involve the direct contact of nanozymes with natural systems. Some CD-based nanozymes do not exhibit biosafety when exposed to the environment. This is because the degree of carbonization affects cytotoxicity. Therefore, it is necessary to have an in-depth understanding of safety protocols for using metal-doped CD-based nanozymes for practical use. Furthermore, metal-doped CD-based nanozymes are less diverse. It is also challenging to achieve high selectivity and specificity like natural enzymes. Multifunctional hybrid nanozymes are complex, too. They require intricate optimization strategies to reach multiple functionalities while maintaining stability and efficiency.

10 Authors' viewpoint about notable drawbacks and suggestions to mitigate them

10.1 Toxicity and environmental impact due to metal leaching, biodegradability, and cytotoxicity concerns

Over time, the leaching of metal ions from metal-doped/metal-hybrid CDs is a must, considering that this limitation can cause significant environmental contamination and toxicity to aquatic organisms. For example, cadmium-doped CDs can potentially release toxic cadmium ions into water bodies to a certain extent. Over time, those leached cadmium ions can significantly bioaccumulate and transport through the food chain and pose serious health concerns to living beings. Likewise, the biodegradability of these metal-based CDs is a crucial concern that leads to long-term persistence in the environment. Such long-term persistence can lead to chronic exposure and adverse effects on the living environment. Moreover, some other metals used in doping, e.g., lead and mercury, are considered cytotoxic and can potentially cause cellular damage and/or DNA mutations.

10.2 Complex synthesis and scalability concerns

Multiple intricate steps, such as high-temperature treatments and the use of chemicals, complicate the production process. For example, fabricating gold-doped CDs requires specific control over reaction conditions, including reaction temperature, pH environment, and concentration of reactants to accomplish the anticipated size and functional attributes. Such complexity confines the scalability of production, as maintaining consistent quality within large batches can be challenging. Furthermore, reaction solvents and reagents can sometimes be toxic, pose safety risks, and require stringent handling and disposal protocols. This additionally poses another scalability concern to be considered effectively. Moreover, the need for specialized equipment and expertise further adds to large-scale production's overall cost-effective ratio and complexity.

10.3 Catalytic efficiency limitations

Compared to natural enzymes, metal-doped or metal-based hybrid CDs, as enzyme mimics, may demonstrate lower catalytic efficiency, which can restrain their effectiveness and deployment in specific applications. For example, CDs are doped with iron to mimic CDs with peroxidase-like activity. However, iron-doped CDs often display decreased peroxidase-like activity owing to the lower density of active sites on their surface as compared to natural horseradish peroxidase. Such catalytic limitations hold back their implementation in pollutant degradation and/or biosensing applications. Though the addition of functional groups or co-doping with multiple metals can help improve catalytic

performance. However, they cause other notable limitations, such as complex synthesis and scalability concerns. To avoid such limitations, understanding the reaction mechanisms at the molecular level can provide deeper insights into designing highly efficient catalysts.

10.4 Stability issues

Metal-doped or metal-based hybrid CDs can experience stability challenges over time due to metal agglomeration and surface deactivation, which may lessen their catalytic efficiency. A notable example is silver-doped CDs that may aggregate owing to the presence of strong van der Waals forces between silver, reducing surface area and loss of catalytic activity. Moreover, impurities or oxidation products cause reactive site hindrance that leads to the surface deactivation phenomenon, further diminishing both catalytic performance and stability. Therefore, ensuring long-term stability needs strategies, e.g., encapsulation techniques, to counteract agglomeration and maintain active surface availability.

10.5 Environmental and regulatory hurdles

Deploying metal-doped CDs in real-time environmental applications encounters substantial regulatory challenges due to potential environmental hazards. Therefore, strict safety assessments are needed to guarantee that these materials do not harm human health or ecosystems. For example, using copper-doped CDs in wastewater treatment must comply with environmental regulations that limit copper concentration to prevent toxicity. Regulatory agencies have been provided with comprehensive toxicity guidelines, environmental impact assessments, and monitoring plans that must be followed to maintain adequate and sustainable processing materials. In this context, collaborative efforts are equally needed by researchers, industry stakeholders, and regulatory bodies to develop standardized protocols and guidelines to limit such environmental and regulatory hurdles.

10.6 Suggestions to mitigate the drawbacks

Several strategies can be adopted to mitigate the drawbacks of metal-doped and hybrid carbon dots (CDs) as enzyme mimics in environmental applications. Firstly, researchers should explore safer doping elements and develop biodegradable CDs to address toxicity and environmental impact to reduce long-term persistence and ecological contamination. For complex synthesis and scalability issues, adopting green chemistry approaches and innovative synthesis methods, such as microwave-assisted synthesis, can simplify production and enhance eco-friendliness. Enhancing catalytic efficiency can be achieved through surface modification techniques, co-doping with multiple metals, and optimizing the doping process to increase the number of active sites. Stability issues can be mitigated by employing encapsulation techniques, such as coating them with protective polymers or silica shells and using metals that form stable complexes. Finally, addressing environmental and regulatory hurdles requires close alliance amongst researchers, industry stakeholders, and regulatory bodies to develop standardized testing protocols and ensure comprehensive safety assessments, enabling smoother regulatory approval and safer deployment of metal-doped CDs in environmental applications.

11 Conclusion and future directions

Carbon dots reveal distinctive properties such as strong fluorescence, high photostability, good biocompatibility, low toxicity, chemical stability, environment friendliness, derivatization ability, easy surface functionalization and enzyme-like activities. Owing to all these properties, the worth of CDs cannot be denied. The physicochemical properties of CDs can be tailored by hetero-atom doping. In this manner, metal doping has been demonstrated to enhance the chemical, electrical, optical, magnetic, and catalytic properties. Its significance involves high quantum yield, sensitive and precise analyte detection, and enhanced catalysis. Among numerous synthetic approaches, the hydrothermal synthesis of metal-doped CDs is more facile. Subsequently, the enzyme mimicking properties of metal-doped and hybrid carbon dots has increased the emphasis on environmental applications. The metal-doped and hybrid CDs nanozymes are stable, reusable, inexpensive, and potent substitutes for natural enzymes even under a wide range of pH, temperature, and concentrations. Among the oxidoreductase enzymes, the peroxidase and oxidase (laccase) mimetic metal-doped and hybrid carbon dots offer more excellent environmental applications such as fluorescent/colorimetric detection and degradation/photodegradation of heavy metals, pesticides, phenolic compounds, organic dyes, and pharmaceuticals (antibiotic-residues). However, the applications for the 'degradation' of pesticides using peroxidase-like metal-doped and hybrid CDs are limited.

Based on the recent reports' studies, the following future directions are suggested: (1) In-depth research is required to enhance the emission wavelength of metal-doped CDs. (2) the construction of fluorescent ratio and signal response is needed for colorimetric and more sensitive analyte detection. (3) precise control over the synthetic process is required to ensure the synergistic interaction of different components within hybrid nanozymes. (4) Research should focus on optimizing the synthesis of metal-doped CDs to further control and improve catalytic activity and stability. (5) Research should underscore the detailed mechanisms of peroxidase-like activity of CDs, identifying the active sites and substrate binding sites. (6) It is essential to explore the diversity, cost-effectiveness, and scalability of producing metal-doped CDs for large-scale environmental remediations. (7) Bioinspiration will be helpful to explore more potentials of metal-doped CDs as enzyme mimics for the degradation of pollutants. In future studies, we expect metal-doped and hybrid carbon dots to be more extensively utilized in environmental applications.

Author contributions

AY: Writing – original draft, Writing – review and editing. MI: Conceptualization, Supervision, Writing – original draft, Writing –

review and editing. MF: Writing – original draft, Writing – review and editing. IA: Writing – original draft, Writing – review and editing. FK: Writing – original draft, Writing – review and editing. RP-S: Writing – original draft, Writing – review and editing. GG-S: Writing – original draft, Writing – review and editing. HMNI: Conceptualization, Supervision, Writing – original draft, Writing – review and editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Generative AI statement

The author(s) declare that no Generative AI was used in the creation of this manuscript.

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Nanomaterials as a new frontier platform: metal-doped and hybrid carbon dots as enzyme mimics for environmental applications

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