

Synthesis of Quantum Dots and Its Application in Heavy Metal Sensing



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Abstract Quantum Dots (QDs) are zero-dimensional nano-particles portraying their distinguishing optical and electronic properties, they are used as nano-sensors. QDs have improved fluorescence characteristics, which comprise photostability, broad excitation spectrum, and narrow emission spectrum. QDs deal with the extensive and sensitive sensing of heavy metal ions ascribed to the presence of distinct capping agents and various functional groups lying outwardly of the QDs. These capping strata and functional moieties attune to the sensing capacity of the QDs, which influences the interactions of QDs with different analytes by various mechanisms. In this chapter, a brief overview of heavy metals as environmental contaminants, their impact on human health, and conventional techniques of detection and underlying modes are first introduced. Then, the role of QDs in sensing heavy metals such as mercury, cadmium, lead, arsenic, chromium, etc., and their progress in the multiplexed determination of heavy metal ions are explored.

Keywords Quantum dots (QDs) · Heavy metal · Sensor · Probe · Human health

1 Introduction

Quantum dots (QDs) are semiconductor nanoparticles with excitons contained in all three spatial dimensions and the ability to transform an entering light spectrum into a distinct frequency of energy output, resulting in different unique optical features. QDs contain distinct energy levels, allowing energy levels to be tuned with small variations in their size, paving way a for various applications like LEDs, photovoltaics, etc. QDs may pass through the bloodstream due to their small size, which unveils up a

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271

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whole new application facet in biomedical applications like biosensing and imaging. QDs portrayed excellent optical properties, as well as a useful surface chemistry, ligand binding capability, and the ability to encapsulate in various materials or attach to various functional moieties besides keeping their native luminescence property, due to their unique photophysical properties. The occurrence of metallic ions in the proximity of QDs has a significant impact on their optical characteristics. Optical equipment can quickly detect even minor alterations in the optical characteristics on the surface of QDs (changes in fluorescence and/or colour), making them great candidates for metal sensors. The sensitivity of a QDs to a certain metal ion causes either an increase in emission or a decrease in QD intensity. Heavy metals are one of the utmost significant pollutants in the environment, and they are rapidly becoming a major issue of concern. Because of its toxicity, non-biodegradable nature, and ability to accrue in the environment, metal contamination in the environment is a severe problem all over the world. Anthropogenic activities such as mining, smelting, industrialization, domestic and agricultural activities, as well as natural activities such as weather, metal soil erosion, and volcanic eruptions, are the primary sources of pollution heavy metal contamination is a major source of concern worldwide, and toxicity caused by a large number of heavy metal ions is far more destructive and severe than toxicity caused by a single metal species. The number of worldwide health risks related to heavy metal exposure has increased [1]. Because of their highly toxic and harmful health effects, heavy metal ions like lead, cadmium, arsenic, and mercury contamination in water has been a grave alarm around the globe. Their accumulation in the human body, agricultural, and aquaculture systems has gained widespread interest in recent years, even at extremely low concentrations. As a result of environmental contamination, the concentration of these unwanted compounds is steadily growing. The root cause is industrial effluents and garbage disposal, both of which end up in the aquatic system. Since they have non-biodegradable nature and hence persists in soil and water for prolonged periods of time, they ultimately damage humans and domestic animals, necessitating their identification and removal from biological and aquatic systems. There are a variety of instrumental methods for detecting heavy metal species, including atomic absorption spectrometry, X-Ray fluorescence spectrometry, inductively coupled plasma mass spectrometry, capillary electrophoresis, and high-sensitivity microprobes, but sample pretreatment, expensive instruments, and the need for trained people to operate these instruments are the real challenges for many of these techniques. As a result, we need a technique for detecting heavy metal ions that is simple, quick, cheap, selective, and sensitive. For metal ion detection, quantum dots have significant benefits over traditional approaches. When metal ions come into contact with the surface of quantum dots, their optical characteristics are very sensitive. Optical equipment can quickly detect slight modifications on the surface of QDs (such as fluorescence or colorimetric changes), making them a good choice for use as a metal sensor.

2 Mechanistic Insight of Human Health Effects of Heavy Metals

Human caused activities such as mining and burning of fossil fuels, heavy metals have been released into the environment by air, water and soil. Bioaccumulation of these metals in living organisms has devastating repercussions. Heavy metals interact with organelles of cell such as cell membrane, endoplasmic reticulum, mitochondria, lysosome, nuclei, and important enzymes actively participating in metabolism and detoxification reactions, leading to DNA damage and conformational changes within cells, paving way for cancer and apoptosis (programmed cell death) in biological systems. In the human body, heavy metals are compartmentalised within cells and tissues of body, here they are attached to proteins and nucleic acids alters their structure and functioning. On the other hand, heavy metal poisoning can have a number of effects on the human body. It can induce mental disease by disrupting central nervous system function, as well as harming blood components and causing damage to the lungs, liver, kidneys, and other vital organs, leading to a variety of ailments. Long-term heavy metal deposition in the body may also slow the progression of physical, muscular, and neurological healing processes, mimicking diseases like Parkinson's disease and Alzheimer's disease. Long-term exposure to many heavy metals ions and their compounds cause mutations, and mimic hormones, disordering the functioning of reproductive and endocrine systems and ultimately causing cancer. Heavy metals and metalloids are among the major environmental contaminants in both aquatic and terrestrial ecosystems. Heavy metals are particularly dangerous at low levels of exposure due to their persistence and bioaccumulation, directly alerting living species on the planet [2] (Table 1).

Table 1 Different limit values of heavy metal concentration set by WHO, EU, EPA (all expressed in mg/L)

Metal ions	EPA	WHO	EU
Silver (Ag)	–	–	0.01
Manganese (Mn)	0.05	0.05	0.05
Copper (Cu)	1.3	1	1
Zinc (Zn)	5	5	0.1
Iron (Fe)	0.3	0.3	0.2
Lead (Pb)	0.005	0.015	0.05
Mercury (Hg)	0.002	0.001	0.001
Chromium (Cr)	0.1	0.05	0.05
Arsenic (As)	0.01	0.01	0.05
Cadmium (Cd)	0.005	0.005	0.005

^a EPA—Environmental Protection Agency

^b WHO—World Health Organization

^c EU—European Union

3 Designing and Development of Sensors for Heavy Metals Toxicity

A range of analytical techniques are used to identify heavy metals. High-performance liquid chromatography, colourimetry, capillary electrophoresis, voltammetry, polarography, atomic emission spectroscopy, inductively coupled plasma emission spectroscopy, atomic emission spectroscopy, and inductively coupled plasma mass spectroscopy. Despite the high selectivity and specific sensitivity of all of these techniques, their use in the sensing of heavy metal ions is restricted due to high costs, time constraints, tough handling operations, the need for technical assistances for sample preparation, and the need for a variety of instruments.

Optical fluorescence-based techniques for sensing heavy metal ions in the environment have gotten a lot of attention since they offer real-time detection without the use of expensive equipment. The exceptional generation of a realistic and resilient fluorescence-based is intrinsically related to the type of the principles on which it is built especially with new breakthroughs in materials to create unique optical fluorescence fluorescence-based. Optical processes like as stroke shifts, fluorescence quenching, energy transfer, and charge transfer are exploited in fluorescence-based detection systems. These are the core concepts that provide sensitivity and selectivity to fluorescence-based sensing systems. Many different probes have been used in fluorescence-based approaches in a range of scientific disciplines, including fluorescent proteins, chemical dyes, and quantum dots [3].

3.1 *Fluorescent Aptaswitch for Heavy Metal Detection*

Aptamers are synthetic oligonucleotide sequences that can preferentially connect to a target molecule. A simple immobilization method, good thermal stability, and simplicity of synthesis and modification are only a few of their enticing properties for sensor design. The most noteworthy characteristic is their outstanding affinity and specificity for each of their target analytes. As a result, aptamer-based detection techniques have risen to prominence as highly selective recognition tools [4]. When thymine (T) interacts with mercury (II) ions, it generates T–Hg²⁺–T base pairs in DNA duplexes, and when cytosine (C) interacts with Ag⁺ ions, it forms C–Ag⁺–C mismatches [5]. Since Ono and co-workers [6] reported the first ON-based Hg²⁺ sensor, T-rich ON sequences have been widely used for the selective detection of Hg²⁺ in water samples [7, 8].

3.2 Heavy Metal Ion Sensors Based on Organic Dyes

Organic dyes are extensively employed in the construction of fluorescence-based sensors because of their attractive qualities like a high value of molar extinction coefficient, strong signal, simplicity of modification, and the existence of several potential reactive sites in their structures. The fluorophores are modified with an ion recognition unit (ionophore) that serves host for the specific metal ion in order to detect heavy metal ions. The interaction between the ionophore and the mark analyte leads to a change in the fluorophore's photophysical characteristics, which leads to a shift in its fluorescence emission, generally from "off" to "on." Mostly, crown ethers, aliphatic and aromatic amines are commonly used ionophores because they operate as electron donors, quenching fluorescence light by a photo-induced electron transfer (PET) mechanism through the fluorophore when the target metal ion is absent.

Rhodamine derivatives are the most widely used organic dyes because of their structure-dependent characteristics. Fluorescein and coumarin derivatives are two more dyes commonly used in the production of fluorescent sensors [9]. Fluorescent dyes have a narrow excitation spectrum, rapid decay, and a low quantum yield. These problems have been solved, and quantum dots can now be used in sensing devices [10].

3.3 Quantum Dots as Probe for Inorganic Metal Detection

QDs show great potential for heavy metal ion detection because of their fluorescence characteristics. QDs are proving to be superior fluorescent probes when equated to different fluorophores such as fluorescent proteins and chemical dyes. In comparison to other traditional fluorophores, QDs have greater brightness, high photostability, hefty stoke shifts, wide absorption spectra, great molar extinction coefficient, high quantum yield, long fluorescence time, photobleaching resistance, size-dependent optoelectronic properties, broad absorption spectra, and tuneable emission spectra. QDs are semiconductor nanocrystals that have lately become popular as fluorescent probes in chemical research, bio-sensing, and bio-imaging [11]. They are used as a new class of fluorescent markers as a substitute for conventional fluorescent markers (organic dyes and fluorescent proteins) due to their excellent and unique optical and electronic properties, such as broad absorption spectra, narrow and tunable emission spectra, long fluorescence lifetime, high photostability, and resistance to photodegradation [12]. The inter-band and intra-band relaxation pathways are altered by the quantum confinement effect. QDs have inspired a lot of interest as fluorescent probes for sensing processes, in vitro and in vivo bioimaging, quantum computers, light-emitting devices, photovoltaics, and, most crucially, analytics-based chemistry. QDs have remarkable electrical and optical properties which can be transformed by lowering the number of atoms present in the QDs beside preserving the chemical

composition. The optical and electrical characteristics of semiconductor nanoclusters are determined by interactions amongst electrons, holes, and their immediate surroundings. When the excitation energy exceeds the bandgap of QDs, electrons move from the valence band to the conduction band, triggering photoexcitation. An electron present in an excited state has a huge amount of energy. A hole and an excited electron make form an exciton. After being recombined, electrons and holes relax to a lower energy state. QD luminescence is caused by radiation relaxation. Recombination and relaxation provide extra energy that might be radiative or non-radiative. The presence of adsorbates on the surface of QDs has been discovered to have an impact on their fluorescence efficiency. They can demonstrate a significant change in fluorescence intensity property when they approach the surrounding molecules, which is utilised in the sensing method [13]. Fluorescence intensity in QDs is caused by combination of the excitation, which in turn is a recombination of charge carriers (electron-holes), and variations in charges present on the surface would influence both the efficiency of electron-hole recombination and luminescence efficiency. Photodegradation and quenching of QD fluorescence intensity are caused by atoms with unmet valencies found on the surface of QDs. To develop QD-derived sensors for selective sensing of heavy metal ions, it's best to modify the surface of the QDs with appropriate capping layer materials and ligand molecules to make them chemically stable and photobleach-resistant [14]. The nature of capping layer and ligands affect the fluorescence response of quantum dots. A number of bifunctional ligands are used to modify the surface of QDs (TOPO, cysteine, PEG, amphiphilic polymer, glutathione, mercaptoacetic acid, thioglycolic acids, peptides, avidin, and streptavidin). These surface ligands can modify their sensitivity and choosiness for explicit analytes of interest by adjusting the fluorescence response of QDs, and this response can be further changed by changing the capping layer. Organic and inorganic materials are used as capping materials for QDs. An organic capping layer facilitates the capacity of QDs to bioconjugate. QDs which are capped by organic ligands are photo unstable, resulting in trap sites owing to weak interactions between the atoms present on the surface and the capping molecules. Inorganic capping compounds aid in the passivation of QD surfaces and the formation of the core-shell structure of QDs [15].

Quantum dots (QDs) finds explicit applications in different fields such as photovoltaics, bioimaging, and light-emitting diodes. Direct interaction between the analyte and the QDs, functionalization of the QDs, and integration of the QDs with other sensory materials are three basic methodologies for developing sensing devices [16]. Quantum dots are extensively used for detection of different heavy metals due to their aforementioned features and unique process. Metals such as mercury, lead, cadmium, arsenic, and chromium are commonly detected.

3.3.1 Detection of Mercury

Mercury (Hg^{2+}) is regarded as hugely detrimental water pollutants by the World Health Organization (WHO) because of its severe impacts on environment and human

health, even at minuscule concentrations. Mercury binds to DNA, interrupting its normal function, and the toxicity is linked to mitosis across the blood–brain barrier. Clinical signs of mercury poisoning include pulmonary edema, minamata sickness, renal damage, chest pain, and chronic central nervous system damage [17]. The World Health Organization (WHO) has set a maximum acceptable amount of 1 mg/L as the upper limit based on these facts. The main factors attributed to their rising level of water resources are emissions from several enterprises and refineries. Polluted water containing mercury must be identified and rectified as soon as feasible.

Zhou and co-workers used CQDs for the detection of mercury for the foremost time. The synthesis of quantum dots was done by EDTA pyrolysis. The attachment of Hg (II) on the surface of CQD is anticipated to bring variations in surface states, paving way for recombination of non-radiative electron/hole pairs. The synthesized pristine material was capable of detecting Hg(II) to a equal of 4.2 nM, which is less than limits set by WHO. The probe was effectively used for real water samples obtained from tap water, lake water, and fountain water and against different ions [18]. Additionally, CDs synthesized from different precursors like sodium citrate, polyethene glycol (PEG), folic acid, and casein were used for the detection of Hg (II) in water with LOD values of 10 nM, 1 fM, and 6.5 nM, respectively.

GCQDs produced from vegetables (Hongcaitai and mushrooms) were used to detect Hg (II) in spiked and unspiked water samples [19–21]. Kaur and co-workers [22] synthesized a glutathione-capped CdS quantum dot with a sensing range of 0.54 nM for detection of mercury. However, the presence of copper and chromium ions obstructed mercury detection, restricting its usage in field applications [22]. Zhang and coworkers [23] used the cooperative effect of Ag₂S and ZnS quantum dots to detect Hg²⁺ electrochemically under visible light, a novel method that combines metal and semiconductor sulphides. Manna and co-workers [24] established a ratio-metric sensor based upon a metal–methyl salicylaldehyde complex capped on ZnS quantum dot doped with Mn²⁺ for identifying Hg²⁺ ions. The presence of the analyte in the sample is indicated by a change in luminescence color [24].

Chu and co-workers [25] designed a mercury detection system based on cerium-doped silicon sulphide quantum dots. The detection method's features include double emission, linear fluorescence dependency on mercury level, and a detection limit of 0.8 m/l [25].

Tanwar and co-workers [26] established white light emission from a combination of silicon QDs and gold nanoclusters, besides its application in mercury ion monitoring and mixture ratio management [26].

Non-metal-based quantum dots also find explicit application in heavy metal sensing. Li and co-workers [27] discussed the application of multimodal carbon dots, both blue and green carbon dots, in the detection of mercury ions with a limit of 50 nM [27]. Wang and co-workers (2019) used UV light to synthesize 1,2 dithioglycol functionalized carbon nitride quantum dots with a quantum yield of 27%, while Sahoo and co-workers [28] deployed spider silk to synthesize environmentally-friendly carbon quantum dots for recognising Hg(II) ions through the FRET mechanism [28].

Graphitic carbon nitride quantum dots (polymeric nanomaterials) for Hg(II) detection via the PL quenching process was described by Patir and Gogoi [29]. A similar

technique was utilised to develop boron-nitrogen co-doped graphene quantum dots for sensing Hg^{2+} and graphene quantum dots [30]. The application of a nitrogen-doped carbon dot for sensing Hg^{2+} with a detection margin of 5.3 nM was investigated by Tadesse and co-workers [31]. Extensive research has been conducted on ratiometric fluorescence sensing of heavy metals such as Hg^{2+} and thymine-rich ssDNA for Hg^{2+} detection [32].

3.3.2 Detection of Lead (Pb)

Lead (Pb) is a heavy metal ion that poses a substantial effect on biological communities, different ecosystem, and human health, even in minute concentrations. Lead has been attributed to hypertension, developmental abnormalities, anaemia, and neurological and reproductive system malfunctions at blood concentrations more than 5 mM. As a result, the USEPA has set a Pb (II) limit of 15 mg/L in drinking water [33]. The detection of different ions, such as Pb (II) and Cu (II) ions, was examined using boron-doped CQDs (B-CQDs) with detection limits of 13.56 and 8.47 nM [34].

In another study, citric acid-based N-CQDs were coupled with Fe_2O_3 to preconcentrate and solid-phase extract little quantities of Pb (II) derived from a matrix of both vegetable and water samples. This method had a linear detection range of 0.062–62.1 mM and a good detection limit of 16.8 mM [35]. Pb (II) sensing in actual water samples was also achieved using fluorometric GCQDs made from *Ocimum sanctum* leaves (LOD-0.59 nM) and *Lantana Camara* berries (LOD-9.64 nM) [12, 36]. Sharma and Mehata [37] used MoS₂ quantum dots to design a tool for lead ion detection based on quenching. This detection approach is delicate, with a detection limit of 50 M, due to dose-dependent fluorescence quenching. Mir and co-workers [38] employed fluorescence quenching to detect lead ions using ZnSe and ZnSe@ZnS core-shell quantum dots capped with thioglycolic acid [38]. Kaewprom and co-workers [39] used dithiocarbamate doped graphene quantum dots to construct a resonant light scattering sensor of complex metallic nanoparticles for the specific detection of lead ions in water samples. Carbon dots with flavonoid moieties are a very sensitive technique with a detection limit as low as 55 pM [19–21]. Another carbon dot-based method developed by Bhamore and colleagues [40] combines glutathione-capped carbon dots with an agarose gel for optical detection with the naked eye [40]. This system has a worthy linear connection with lead content and does not require a lot of heavy instrumentation for detection, making it appropriate for a field application.

3.3.3 Detection of Chromium (Cr)

The presence of high quantities of chromium in water supplies is mostly attributable to modern-day businesses (e.g., bronzing, mining, electroplating, and textile dyeing). Cr (VI) is a well-known metal that has been linked to carcinogenic and mutagenic health consequences, posing a hazard to ecological systems. According to the USEPA, total

chromium in drinking water has an acceptable limit of 100 ng/ml, while Cr has a limit of 50 ng/ml. The inner filter effect and static quenching processes are also examined in relation to Cr sensing approaches employing CQDs. A detection limit of 24.6 mM for Cr (III) sensing was achieved using yellow fluorescent CQDs (y-CQDs) produced by acid carbonization of sucrose in the presence of phosphoric acid as a dehydrating agent [34].

Elmizadeh and co-workers [41] deployed a fluorescence quenching method based on synthetic ligand coated CdTe quantum dots to design a sensitive nanosensor for quick detection of Cr(III)ion [41]. Parani and Oluwafemi [42] investigated an aggregation-based quenching method for the selective detection of Cr (III) ions using AgInS₂-ZnS quantum dots [42]. This sensing system used the collaborative effect of static and dynamic quenching to differentiate Cr(VI) from Cr(III) in mixed samples [7, 8]. Khan and co-workers [43] presented a ZnO quantum dot-based sensor for the selective detection of Cr⁶⁺, with a detection limit of 0.18 nM [43]. Mondal and co-workers [44] make use of a white light-emitting Eu and Tb co-doped carbon fluorescent sensor for the detection of Cr(VI) ions [44]. Hu and co-workers [45] developed chlorine and nitrogen co-doped carbon nanodots for the speedy detection of Cr(VI) ions, and CQDs fluorescence was quenched using a combination of dynamic quenching and the inner filter effect [45]. Wang and co-workers [46] used a similar co-doping approach for selective detection of Cr³⁺ ions with a detection limit of 6 M by means of doping S/N in carbon dots [46]. A fluorescent probe for detection of Cr³⁺ with a limit of detection as low as 0.02 M was also designed deploying a carbon graphene allotrope.

3.3.4 Detection of Cadmium (Cd)

Cadmium (Cd) is a well-known non-essential human body component. Cd is used in sectors such as bronzing, storage batteries, plastic stabilisers, waste metal treatment, dyeing, colorants, nuclear reactor rods, and semiconductor manufacture. Cadmium uptake beyond the tolerance limit (5 mg/L) has been associated with deadly diseases such as itai-itai, prostate, kidney, and lung cancers, among others. An electrochemical sensor based on N-CQDs-graphene oxide hybrid (NCQDs-GO) was designed for numerous ion detection of lead and cadmium ions by deploying anodic stripping voltammetry [47, 48]. Because of greater electro-agile surface area and plenty of oxygen-rich functional surface moieties, the hybrid expedited the specific detection of Cd (II) and Pb (II) ions through electrostatic force, which further amplified the detection limit of the improved electrode (Cd (II): 834 mM; Pb (II): 1420 mM). CQDs also find application as a luminophore for Cd (II) detection in graphite furnace atomic absorption spectroscopy. Yin and co-workers [49] described a CdTe/CdS quantum dot inscribed with ammonium pyrrolidine dithiocarbamate, which leads to structural changes in reacting with Cd ions, causing dot quenching. The Cd ions are attached to the changed surface, restoring fluorescence and letting for effective Cd ion detection [49]. The presence of Cd ions in the material analyzed causes a variation in the ZnSe quantum dot, generating a ZnSe/CdS core-shell structure. This approach exhibited

high selectivity for Cd ions, with a detection limit of 11 nM [50]. Pandey and co-workers [51] synthesized carbon dots using green technology which detect Cd (II) ions via ligand-mediated electron transfer in *Murraya koenigii* leaves. This approach may detect cadmium ions in the least value of 0.29 nM [51].

3.3.5 Detection of Arsenic (As)

Humans are prone to arsenic directly or indirectly by the absorption of contaminated water, as well as foods and crops that have been irrigated with arsenic-rich water. According to the World Health Organization, arsenic-related health problems impact up to 140 million people in around 50 nations. The inorganic form of As (III), also accepted as arsenite, is the utmost lethal of the various oxidation forms of arsenic because of its kinesis in water and is readily uptaken by cells. Skin damage (pigmentation, lesions, patches, and other symptoms), cardiovascular sickness, and skin, lung, and bladder cancer have all been associated with long-term ingestion of arsenic-contaminated water [52]. As a result of these observations, WHO has set an acceptable limit of 10 mg/L. Microwave-based pyrolysis of citric acid and sodium thiosulphate produces sulfur-doped CQDs that can be used in dual info systems, such as colorimetric and fluorescence, to detect inorganic As (III). The addition of glutathione to the SCQDs improved the sensor materials' selectivity for As (III). In fluorescence mode, these modified S-CQDs had detection limits of 32 and 48 pM, respectively, in water samples obtained from river water and tap water [53]. CQDs synthesized from decaying tomatoes and prickly pear cactus have recently been described for detecting As (III) in pond, tap, river, and industrial water samples. Pathan and colleagues [54] created a 'turn-on' sensor based on magnetic graphene oxide quantum dots for the selective detection of As^{3+} ions [54]. An analogous mechanism was studied by Wu and co-workers [55], in which CdTe/CdS core-shell quantum dots capped with cysteine make coordinating interaction with the arsenic ions, resulting in dots aggregating. This technique displayed high sensitivity and selectivity with a detection limit of 10 ng/L [55].

3.3.6 Detection of Copper (Cu)

Isarov and Chrysochoos [56] proposed a method for determining Cu^{2+} content and describing the mechanism of action using CdS QD. Cu^{2+} interacts rapidly with CdS QD surfaces, stimulating the core conduction band excitation state electrons, leading to recombinant valence band holes [56]. It would result in QD fluorescence quenching and a redshift emission peak. Xie [57] enhanced the QD modifier by coating the ZnS-coated CdSe core shell QD (CdSe/ZnS QD) surface with bovine serum albumin (BSA). So they detected Cu^{2+} and copper in Chinese herbal medicine using QD-BSA light probes [57]. Yan and co-workers [58] used cysteine and glutathione as modifiers to manufacture CdTe QDs and obtained quantitative Cu^{2+} detection with 0.15 g L^{-1} LOD. In this, Cu^{2+} binds to the surface of CdTe QDs via coordinated

actions initiated by the surface's abundant carboxyl amino groups. Then it's reduced to Cu^+ , which causes fluorescence to fade [58].

3.3.7 Detection of Silver (Ag)

CdS quantum dots were synthesized using L-cysteine-cysteine. QDs on interaction with AgC, produced fluorescence enhancement which could be ascribed to CdS/AgC SR complexes. Fresh L-cysteine was added on to improve imperishability. The sensitivity of this method has been improved, with a LOD of 5×10^{-9} mol/L. Xia [59] tailored water-soluble CdTe QD of four varying sizes (19, 26, 31 and 42 nm) followed by coated of mercaptopropionic acid and studied the interactions between CdTe QD of different sizes and AgC [59].

3.3.8 Miscellaneous Metal Ion Detection

Li and coworkers [60] developed CdTe QD coated with thiol and nano-rods for bivalent metal ions such as Co^{2+} , Ca^{2+} , Mg^{2+} , Zn^{2+} , Mn^{2+} and Ni^{2+} . In this study, fluorescence enhancement was caused by Zn^{2+} , whereas fluorescence quenching was caused by Mn^{2+} , Ni^{2+} , and Co^{2+} [60]. Na and Ming [61] created CdTe QD modified with thioglycolate and discovered that the mechanism could be linked to the coordination bond formed between hydroxyl and carboxyl groups and ions, besides other characteristic groups present on the surface of the QDs. This approach can be used for detection of vanadium in water samples in traces. Ali and co-workers [62] synthesized glutathione modified CdTe and CdSe/ZnSe QDs for the quantitative detection of fluorescence quenching Pb^{2+} with a LOD of 20 nmol L^{-1} [62].

3.3.9 Multiplexed Detection of Heavy Metals

Singh and colleagues [63] synthesized CdSe QDs which are capped with starch for collective detection of Cr along with Hg in aquatic environments. The capacity to determine the oxidation state of the analyte and the ease of synthesis are distinct features that make it a feasible field application alternative [63]. On the basis of quenching, Zhou and co-workers (2019) established a microfluidic system based on ZnSe quantum dots for the specific detection of lead and cadmium. Because of its eco-friendly nature, low cost, and high efficiency, this device is a viable alternative for field application. A comparable approach using SnO QDs for effective detection of Hg^{2+} and Pb^{2+} ions in water was discovered by Liu and co-workers [64]. Another quenching-based detecting technology is CdTe QDs which are capped with mercaptopropionic acid [65]. To detect Pb, Cr, and other metal ions, Baslak [66] employed hydroxylated CdTeS QDs coated with cetyl tri ammonium bromide. This technique had a higher sensitivity for detecting Cr (III) ions [66]. Radhakrishnan and colleagues

[67] synthesized a carbon dot–graphitic nitride-based nano-composite with fluorescence recovery in the presence of lead and chromium. This turn-on sensor depicted greater specificity and sensitivity, with detection limits of 0.2 nM, and 0.54 nM for Lead and Chromium, respectively [67]. Chini and co-workers [68] designed a FRET-based graphene quantum dot-carbon dot system for the detection of As^{5+} , Pb^{2+} , and Hg^{2+} , in which non-radiative energy transfer to carbon dots which is an acceptor causes donor-graphene dots (donor) to quench [68]. Yarur and co-workers [69] used carbon dots to construct a ratiometric detection system for the sensing of Pb^{2+} and Hg^{2+} ions, with detection limits of 37.1 and 39.5 nM, respectively [69]. Buledi and co-workers [70] studied a range of nanomaterial-based sensors for multiplexed detection of heavy metals like mercury and lead, using both metal and non-metal-based QDs [70] (Table 2).

4 Important Trends and Challenges in Present Scenario

This chapter presents big picture on the different quantum dots with special emphasis on carbon dots and their current development in the optical diagnosis of key environmental contaminants (heavy metal ions) divulges their intensified progress in topical past. Still, many tasks until now must be considered for their probable reliability and application as practically feasible sensing probes in daily life. Synthesis approaches for emerging highly stable and effective quantum dots, along with the emission from the total visible spectrum and fine bandwidth of fluorescence signal is essential for precise applications and improved sensitivity. Chemically tailored QDs have high quantum yield and FL signal intensity in comparison to green QDs. Particularly, research is in progress to find the probable inexpensively feasible methods for purification of green QDs. Numerous less explored workable precursors such as recycled waste, microbes, and residuals, are lined up for assessment of synthesis of QDs of natural doping with greater quantum yield. Above and beyond the mandatory mechanistic apprehension of green QDs synthesis, it is crucial to recognize the cause responsible for the precursor-predicated precision of the QDs for explicit heavy metal ions. On the contrary, a synchronized and upfront surface alteration might upsurge optical signal for improved pertinence. Further comprehensive studies are needed for development of a ratiometric and recyclable (by operationalizing QDs onto 2D/3D substrates) sensing probes exhibiting FL emission in the UV–visible-NIR range. We have faith in up-coming inquisition of optical detection-based systems deploying carbon dots will procure wide-ranging consideration in different fields such as agriculture, food, and textile pollutant sensing owing to its easiness, biocompatibility, profitable.

Table 2 CQD sensors for heavy metal detection in water

Metals	Carbon QDs	Source	Sensing tactics	Detection range	Detection limit	References
<i>A. Mercury</i>						
	CQDs	Lake water, tap water and fountain water	Fluorometric	0–3 μm	4.2 nM	Zhou et al. [18]
	CQDs	Tap and lake water	Fluorometric	1–10 μm	1 fM	Yan et al. [71]
	Ag-CQDs	Tap and lake water	Fluorometric	0.5–50 μm	85 nM	Liu et al. [72–74]
	CQDs	Aqueous solutions and real water	Fluorometric	6–79 nM	2.1 mM	Choudhary et al. [75]
<i>B. Arsenic</i>						
	CQDs	Aqueous solutions and real water samples	Fluorometric	–	0.2 μM	Saikia and Karak [76]
	S-CQD	Aqueous solutions	Colorimetric	–	32 pM	Gupta et al. [53]
	Thiol functionalized CQDs	Aqueous solutions and Real water samples	Fluorometric	0.1–200 mM	17.2 μM	Pooja et al. [77]
	GSH-CQDS	Aqueous solutions and real water samples	Fluorometric	2–12 nM	2.3 nM	Radhakrishnan and Panneerselvam [78]
<i>C. Iron</i>						
	N-CQDs	Living cells	Fluorometric	1–250 μM	0.52 μM	Song et al. [79]
	N,P-CQDs	Tap water	Fluorometric	0.05–200 μM	0.05 μM	Guo et al. [80]
	GCQDs	Aqueous solutions and real water samples	Fluorometric	0.02–40 mM	0.13 μM	Liu et al. [72–74]
<i>D. Copper</i>						
	B,N-CDs	Natural water samples	Fluorometric	1–25 μM	0.3 μM	Rong et al. [81]

(continued)

Table 2 (continued)

Metals	Carbon QDs	Source	Sensing tactics	Detection range	Detection limit	References
	Needle like calcium phosphate/carbon dot hybrid composites	Drinking water	Fluorometric	10–20 μM	9.82 μM	Guo et al. [82]
	CQDs	Aqueous solutions	Fluorometric	0.33–66 μM	4.8 μM	Ma et al. [83]
<i>E. Lead</i>						
	CQDs	Aqueous solutions	Fluorometric	–	4.6 nM	Liu et al. [72–74]
	N-CQDs conjugated with Fe_3O_4	Water and vegetable samples	Solid phase extraction	0.062–62.1 mM	16.8 μM	Mashkani et al. [84]
	CQDs	Aqueous solutions and real water samples	Fluorometric	0.033–0.67 μM	12.7 μM	Liu et al. [85]
<i>F. Cadmium</i>						
	CQDs/AuNCsnanohybrid	Aqueous solutions and real water samples	Ratiometric Fluorometric	0–250 μM	32.5 nM	Niu et al. [86]
	NCQDs	Aqueous solutions and real water samples	Solid phase extraction	–	201 nM	Li et al. [19–21]
<i>G. Zinc</i>						
	Quinoline/CQDs	Aqueous solution	Fluorometric	–	6.4 nM	Zhang et al. [87]
	Quercetin/CDs	Aqueous solutions and living cells	FRET	2–100 μM	2 μM	Yang et al. [88]
	CdTe QDs/CQDs	Aqueous solutions and biological media	Ratiometric Fluorometric	0.50–40 μm	0.33 μM	Song et al. [79]
<i>H. Chromium</i>						
	CQDs	Environmental water samples	Fluorometric	5.1–612 mM	1.53 mM	Vaz et al. [89]

(continued)

Table 2 (continued)

Metals	Carbon QDs	Source	Sensing tactics	Detection range	Detection limit	References
	N, B-CQDs	Real water samples	Fluorometric	0–250 mM	0.5 mM	Guo et al. [90]
	N, P-CQDs	Lab prepared aqueous samples and biological samples	Fluorometric	4.2–31.7 mM	1.2 mM	Singh et al. [91]
<i>I. Selenium</i>						
	N-CQDs	Aqueous solutions and living cells	Fluorometric	0.2–30 mM	23 nM	Devi et al. [92]
	CQDs	Aqueous solutions and real water samples	Fluorometric	0.007–2 mM	0.78 mM	Wang et al. [93]

5 Probable Steps for Improving Sensitivity and Selectivity of Individual Metal Ions

Suitable unpretentious and handy functionalization procedures, without mislaying the biological, optical, and chemical properties of the nanoparticles, are needed to augment discrimination and sensitivity of QDs toward various heavy metal ions. Beside this, the application of maintainable genetically modified biomass with precise metabolic paths can assist in the designing of finger-printed response based on optical sensing. Like specificity, signal intensification is the unswerving process for enlightening the sensitive nature of optical sensors. Specifically easy-going and projecting ways to expand the signal strength is by passivating the QDs with various polymer-based operationalization procedures. Therefore, equilibrium amid the selectivity and sensitivity protocols can be attained. Furthermore, metal/semiconductor nanoparticles functioning as a carrier for CQDs active species might conceivably consequence in needed optical characteristics. These nanoparticles will be attaining an improved signal amplification and function as an supersensitive optical sensor for sensing analytes. There is a style for mini and simplification of detection by portable and mini devices which deliver quick and precise responses with probable importance in the point-of-care technologies. Hardware and software can be united with detection measures like colorimetric assessment and luminescent assays using portable devices adequately.

6 Concluding Remark

Escalating anthropogenic activities are responsible for releasing heavy metal pollutants in natural aquatic and soil systems, and which poses a substantial menace to human and environment. Taking into account the grave health and environmental issues of these lethal and non-biodegradable metal ions, there is immediate need of solutions like monitoring in aquatic system. Optical-chemical sensors of nano-dimensions have undeniably shown higher sensitivity and specificity for these contaminated metal ions. Yet, there is demand of environment friendly and workable sensor material in this area. Quantum dots are low-priced, ecologically friendly, biocompatible, and exhibited improved properties, and hence are considered as superior nanomaterials for sensing of heavy metals. This chapter has been systematized to brief the attempts made in the development of QD sensing systems with prime focus on the present status, challenges, and future prospects. This chapter will benefit the researchers, technologists, and engineers to scale up both biological and chemical synthesis methods along with establishment of outstanding visual color-based sensing techniques. Simplicity in designing and augmentation of specificity towards target metals needs upgradation in their performance, selectivity, and sensitivity. To conclude, challenges concerned with QD-based disposable sensors and user-friendly readout systems needs extensive investigation to inflate their use in real-world sensing

applications. The field applicability of the sensors will offer feasibility in onsite metal detection and the work hassle free. It will also impart incessant monitoring of metals ions conceivable on the locations selected for observation.

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