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REVIEW

Principle, design, strategies, and future perspectives of heavy metal ion detection using carbon nanomaterial-based electrochemical sensors: a review

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Abstract
Developing a fast and easy method to detect the presence of heavy metal ions is all time necessity since the highly poisonous nature of these metal ions makes them awfully dangerous to the atmosphere and living beings. Among the different sensing techniques, the electrochemical technique offers several advantages such as fast detection, high sensitivity, and lower detection limit. Out of various electrochemical techniques, voltammetry is commonly used in the identification of heavy metal ions in various environmental conditions due to its high precision and sensitivity. Here in, carbon-based nanomaterials outplay other materials used for electrode modification due to their exceptional properties. Keeping this in mind, this review discusses the latest advancements in electrochemical sensors for detection of heavy metal ions based on a number of carbon-based nanomaterials, primarily carbon nanotubes, carbon quantum dots, graphene and its derivatives, and graphene quantum dots. Further, the physical and chemical aspects of various electrochemical sensing platforms for detecting heavy metal ions are also addressed.

Keywords Heavy metal ions · Electrochemical sensor · Voltammetry, biodegradable

Introduction

Nowadays with a large population concentrated in urban areas, there is an increasing demand to provide them with clean drinking water. The growing population, anthropogenic practices, rapid industrialization, and amateurish use of natural water resources have adversely affected the quality of water. Hazardous heavy metals, narcotics, insecticides, and dyes, which are responsible for the pollution of water, are the by-products of rapid industrialization and unhealthy farming practices [1–11]. With growing demand for clean water, it has become imperative to find appropriate ways to purify water and ensure reusability [12–15]. Chemicals from agricultural and/or domestic waste, cosmetics, and fertilizers are the main sources of heavy metal ions (HMIs). Among the heavy metals found in the atmosphere, arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), and mercury (Hg) are toxic and oncogenic and their exposure even in limited amounts may cause severe health problems [17–19]. Lead is a toxic heavy metal that reaches our bloodstream through drinking water. Lead tubing, switches, and so on are the main sources of lead in drinking water. Exposure to high concentrations of lead can lead to cancer, kidney failure, weakening of the nervous system, and mental instability [15, 20–23]. Chromium is another harmful and poisonous metal. It occurs as Cr^{3+} and Cr^{4+} in nature and typically found in minerals such as ferric chromite, crocoite, and chrome ochre (Cr_2O_3) [24, 25]. Cr^{4+} is very toxic and found in waste sewage of textile industries. It is a cause of significant health conditions including kidney injury

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[26–29]. Thus, the potential source of chromium in drinking water is the leakage of commercial wastewater in to water resources. Cadmium, another hazardous heavy metal contaminant, is predominantly found in concrete, paint, plastics, and nickel–cadmium batteries [30–32]. Arsenic, which is a major cause of cancer, vascular diseases, and diabetes, occurs in water due to anthropological practices such as mining, processing, and metallurgy [33–37]. Highly toxic and non-biodegradable mercury exists in different states and types, but even the simple type is harmful to the environment. Mercury discharged from ores is deposited in water and the outer soils of the earth. Mercury is released into the environment; it can be highly mobile, passing between the surface of the earth and the atmosphere. The possible toxic effects of mercury include damage to the liver and reproductive organs, adverse effect on and other health complications. Copper which has a multitude of users in manufacturing and agriculture is a potential source of toxicity [38–42]. Overconsumption of copper causes severe complications, such as elevated blood pressure, kidney and liver injury, spasms, vomiting, or anemia [21, 43, 44]. Though zinc plays an important role in the regulation of certain chemical processes and tissue functions in animals its presence in the presence of zinc in surplus amounts, causes health issues such as skin inflammation, discomfort, nausea, and anemia. Zinc is introduced into the atmosphere by farming operations, groundwater, production of wood pulp, the manufacturing of newsprint paper, and zinc and brass metal works [45].

The HMI concentrations in drinking water as set by the US Environmental Protection Agency (EPA) and the Central Pollution Control Board of India (CPCB) are shown in Table 1. In India, allowable limit for the release of industrial effluvium into domestic land and open drainage has been specified and therefore, it is of utmost importance to track the levels of hazardous heavy metals with appropriate approaches that are sensitive and selective and as well economically feasible [46–48]. Different analytical techniques such as ultraviolet spectrophotometry [49], atomic absorption spectrometry [50–54], atomic fluorescence spectrometry [55–57], high-performance liquid chromatography [58–60], inductively coupled plasma optical emission spectrometry [61–63], X-ray fluorescence spectrometry [64, 65], and electrochemical techniques have been widely used for the effective sensing of toxic HMIs. Electrochemical sensors are widely used for heavy metal detection due to their features such as sensitivity, selectivity, and low cost [70–72]. Detection is based on the change in electrochemical parameters such as current, potential, voltage, and electroluminescence based on the presence of metal ions. These parameters can be related to the amount of electroactive metal ion species present. The electrochemical methods are categorized by the electrical signals they measure into potentiometry, amperometry, chronocoulometry, and voltammetry [17].

Table 1 Standard rules set by US EPA and Indian CPCB for the concentration of the HMIs in drinkable water [46, 47]

Heavy metals	Drinkable water (mg/L)		Maximal limit allowed for industrial sewage releases in India (mg/L)	
	Indian standard*	US EPA (μL)	Into domestic surface	Into public drains
Mercury	0.001-NR	0.002	0.01	0.01
Cadmium	0.003-NR	0.005	2.0	1.0
Arsenic	0.01–0.05	0.010	0.2	0.2
Lead	0.01-NR	0.015	0.1	1.0
Chromium	0.05-NR	0.1	0.1	2.0
Copper	0.05–1.5	1.3	3.0	3.0
Iron	0.3-NR	0.3	3.0	3.0
Zinc	5.0–15.0	5.0	5.0	15.0

*The required rate is set to be the lower limit and the upper limit is allowed only in the deficiency of other possible resource. *NR* no relaxation

The research on carbon-based nanomaterials (CNs) has entered a pioneering stage from macro-level to nano-level with the advancement in nanotechnology. Carbon has different allotropes such as carbon nanotubes (CNTs), carbon quantum dots (CQDs), graphene and its derivatives, and graphene quantum dots (GQDs). Compared to other nanomaterials used in electrochemical applications, carbon has a number of advantages because of its excellent physicochemical properties such as chemical inertness, large surface area, wide potential window, good biocompatibility, unique electronic properties, improved electrocatalytic activity, and ease of functionalization. Being cost-effective as well as eco-friendly, CNs can replace expensive electrode materials with the comparable and promising results [73]. The ease of functionalization of CNs enhances their potential applications in electrochemical sensing. An electrochemical sensor is a device in which a target species is integrated within or connected with a physical transducer called an electrode that transmits the analytical signal to an electronic circuit for the purpose of sensing the target species. It has been established that CNs can upsurge the effective area of the electrode, improve the transfer rate of electrons between the electrode and analytes, and effectively act as catalysts to augment the efficacy of electrochemical reactions. Recently these have been reports of CN-modified electrochemical sensors with higher sensitivity, lower limit of detection (LOD), and very fast electron transfer capacity as compared to traditional electrodes. Hence, we deem it necessary to analyze

recent research to make a quantum leap in CN-based electrochemical sensing applications [74, 75]. Since the field of electrochemical sensors is very broad, this review highlights the physical and chemical aspects of different electrochemical studies for selective detection/of HMIs and a schematic representation of the same is given in Fig. 1. To be concise, only specific instances from each material are illustrated and addressed.

Electrochemical sensor: physical and chemical aspects

The chemical sensor is an instrument that converts the data obtained from the chemical reaction of the samples to be analyzed or from the physical properties of the system considered into an effective signal. Chemical sensors typically consist of two elementary practical elements, comprising a receiver and a transducer [76, 77]. The main function of the receiver is to impart the sensor a high degree of selectivity. The transducer component is accountable for the device's sensitivity. Electrochemistry plays a vital role to meet the demands state by quickly developing technical and industrial research. It encompasses one or a combination of electrochemical methods for observing target species. In a chemical reaction, the electrons travel between the electrodes dipped in an electrochemical cell having an analyte. Analyte composition is found out by measuring and analyzing the current and potential that occur via oxidation reduction reactions. The movement of electrons between the two species in a redox reaction generates electrical energy. Alternatively, electrical energy can force the electrons to move between two chemical species to create a redox reaction. As the electrons move between two species, one of it receives electrons and undergoes reduction whereas the other loses electrons and becomes oxidized. These reactions occur simultaneously, resulting in oxidation–reduction reactions or redox reactions [78]. Electrochemical sensors enable the user to observe the physical and chemical transformations in a sample via quantifiable electrical signals [79–82]. A typical experimental system generally consists of an electrolyte and an electrode-containing electrolyte cell. Here, an aqueous solution comprising HMIs acts as the electrolyte of the system. At the interface of the electrode and electrolyte, the potential of the cell is measured.

A typical three-electrode electrochemical sensor (Fig. 2) consists of a sensing electrode called a working electrode (WE), a counter electrode (CE), and a reference electrode (RE). The WE are normally adjusted to improve the limit of detection (LOD) and sensitivity with different polar materials [83]. The current flow is usually between the WE and the CE. By means of certain glass dividers the CE is separated from the WE. (Its material is chosen so that it does not affect the WE.) A high-input impedance system helps to determine the potential between the WE and RE. The cell is connected to an electrochemical workstation by these electrodes. The

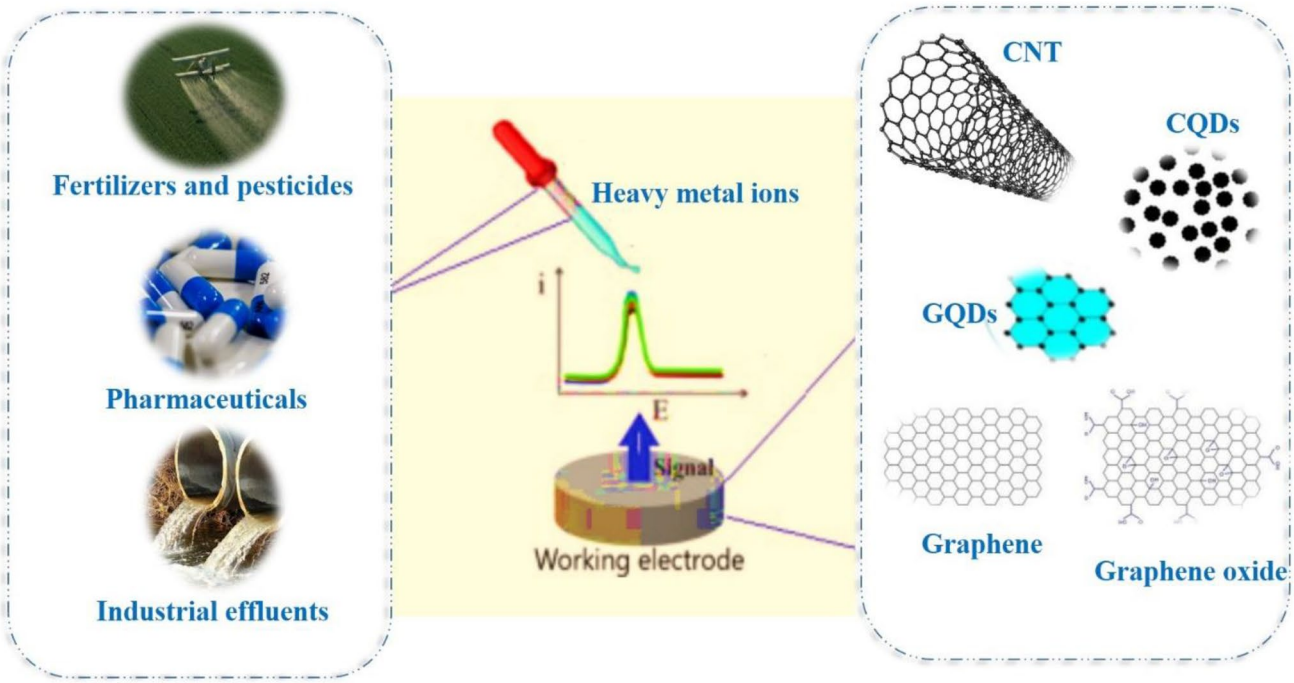

Fig. 1 Schematic representation of heavy metal ion detection using carbon nanomaterial-based electrochemical sensor

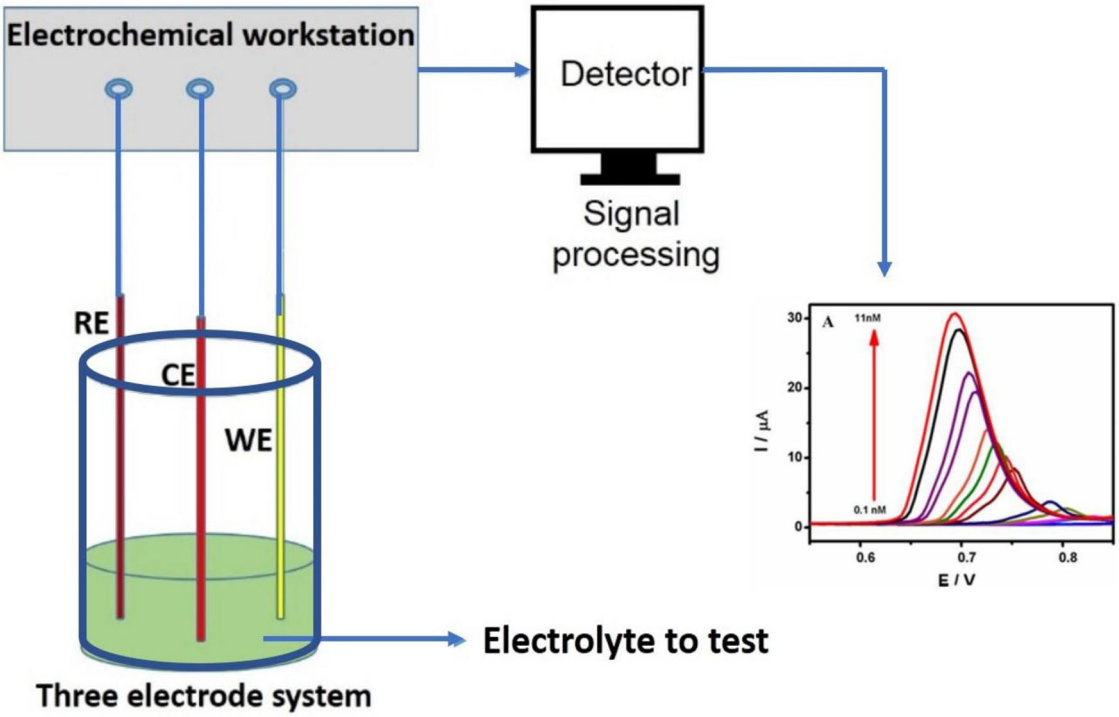

Fig. 2 Schematic representation of an electrochemical sensor

electrodes connect to an electrochemical workstation which in turn connects to a computer setup with the necessary program stages (Fig. 2) [16].

The determination of HMIs involves electrochemical approaches, which are categorized on the basis of the different electrical impulses generated within the solution. Different electrical variables such as current, charge, electrochemical impedance, electroluminescence, and voltage result in the detection of traces of HMIs [83, 84]. The classification of certain heavy metal detector electrochemical sensors is shown in Fig. 3.

Amperometry is a potentiostatic technique that uses a potentiostat, which controls the potential to maintain a difference in potential between the RE and CE. In this system, minute currents are regulated by a non-mercury WE and measured at a constant potential. In an aqueous medium containing electroactive species, amperometry uses a potential phase impulse to be delivered between the RE and WE. Subsequent reductions at the electrode interface, due concentration on differences, induce tremendous current flow. In the time domain, the resulting current is recorded. This technique, however, faces the limitation of detecting only one particular element at a time [16].

Potentiometric methods measure electroactivity in a solution instead of analyte concentration and is a widely used technique due to cost-effectiveness, small response time, good selectivity, and wide-ranging response. This method quantifies the potential at current $I=0$. The limitations of these techniques, viz., high LOD and complexities in developing electrodes, could be decreased with the use of CNs as the contact medium for WE in mixing and hence turns out to be a potential research area for CNTs and metal nanoparticles [85–87].

AC voltammetry and electrochemical impedance spectroscopy (EIS) are the most widely used techniques to study the concentration of analytes in an aqueous solution. Between these two approaches, EIS is used to define the necessary interface characteristics that could be used in sensing [88]. EIS refers to the response of a network to an alternating current or voltage in the frequency domain. The current flow due to an electrochemical reaction results in the transition of charge, which then releases both faradaic and non-faradaic constituents [89].

The technique of chemiluminescence involves chemiluminescent species produced as a result of electron transfer including generation of free radicals in certain cases. In some solutions, these techniques are also used to find a single metal ion dependent on fluorescence emission, which is highly sensitive (parts per billion/trillion), modest, and inexpensive [16].

Voltammetry, due to its high precision and sensitivity, is a key electroanalytical method widely used in the detection of HMIs in different environments. Voltammogram is represented by the current vs. potential or potential vs. time curve,

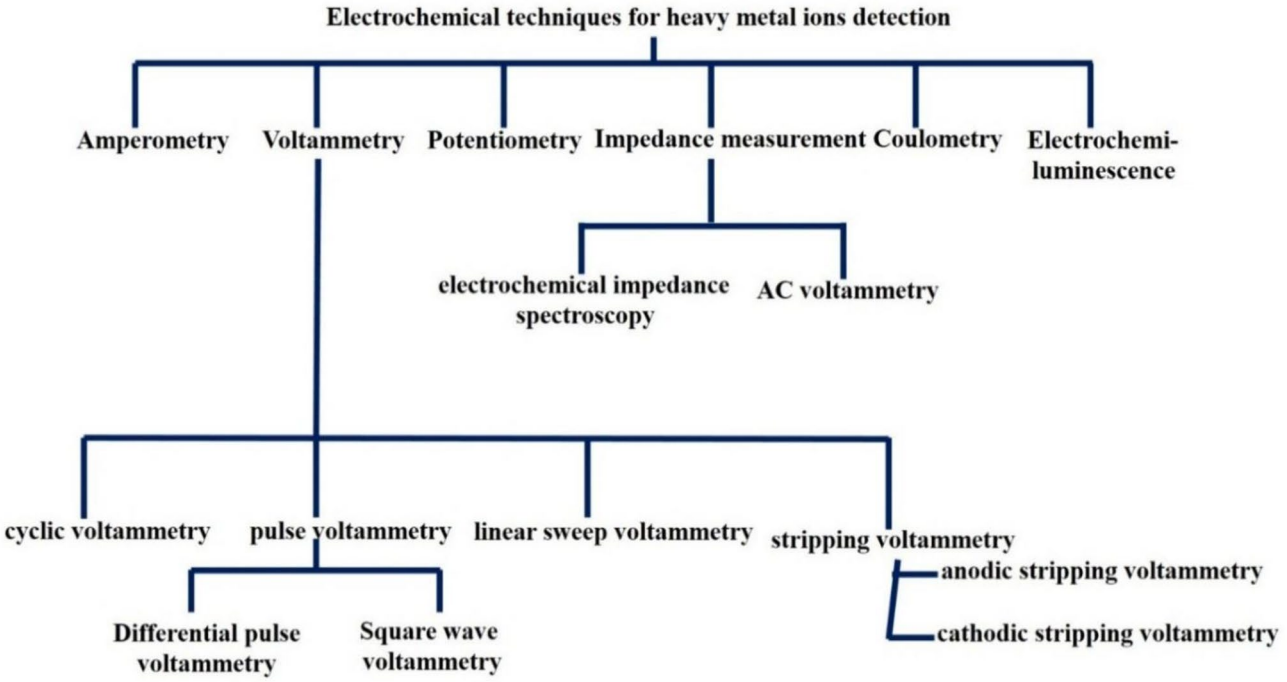

Fig. 3 Classification of different electrochemical sensors for heavy metal ion sensing

that is, it denotes the current measurement of the operating electrode when a potential is applied over a small range controlled by the substrate of the electrode, the auxiliary electrolyte, and the RE [78]. These methods are sufficient for moderately subduing the background current and increasing the LOD. Linear sweep voltammetry is the use of typical electrodes to conduct these experiments using a linear sweep of potential (10–1000 mV/s) to find the resulting current–potential curve (LSV). The analysis that involves a dual potential phase which induces current inversion is called cyclic voltammetry (CV) and that using signal pulse with different profiles and amplitudes is called as pulse voltammetry. Of the different pulse voltammetry techniques, differential pulse voltammetry (DPV) and square-wave voltammetry (SWV) are the most commonly used because of their great sensitivity and the suitability for minute-level analysis. In SWV, HMIs are detected in one step as the metal ions get sorted on the active spots of the electrode. Sensitivity, on the other hand, is improved by using two-step stripping techniques. The techniques are very efficient in detecting accumulation of HMIs for a given period in presence of an applied potential. The technique also has the advantage that five to six sample experiments can be performed at the same time up to sub-ppb level [47]. Stripping voltammetry can be classified into anodic and cathodic stripping voltammetry (ASV/CSV) depending on whether anodic potentials scan or cathodic potential scan is done. Very low LOD (picomolar range) is obtained with ASV method, which is a frequently used electrochemical method for the effective study of metals ions. In the ASV method, the metal ion (M^{n+}) is reduced to M^0 on the application of negative potential [90]. ASV mechanism includes a two-step route (Fig. 4) that consist of cathodic reduction of free metal ion into its zero-valence metallic state on the surface of the electrode. This step is known as the electrodeposition or accumulation. The accumulation is done using a potential that is more negative than that of the M^{n+}/M^0 redox pair for an appropriate time duration under regulated and known mass transfer conditions. This is the preconcentration step. To increase the LOD, the rate of deposition is increased. The analysis of stripping peaks of oxidative step in the current–potential curve is used to define the concentration of metal experimentally. The modest technique of executing the stripping step in ASV is through sweeping of current linearly in the direction of anode. The potential at which the stripping peak occurs and the area under the peak (for a standard linear sweep) shows the charge dependency on the chemical characteristics of the species and quantity of metal deposited [91].

For CN-based working electrode, the mechanism is as follows [92]:

Step 1: Accumulation

CN-based working electrode surface + M^{n+} (aq) + $ne^- \longrightarrow$ (M^0–CN-based working electrode)

Step 2: Anodic stripping

(M^0 –CN-based working electrode) $\longrightarrow$ M^{n+} (aq) + CN-based working electrode surface + ne^-

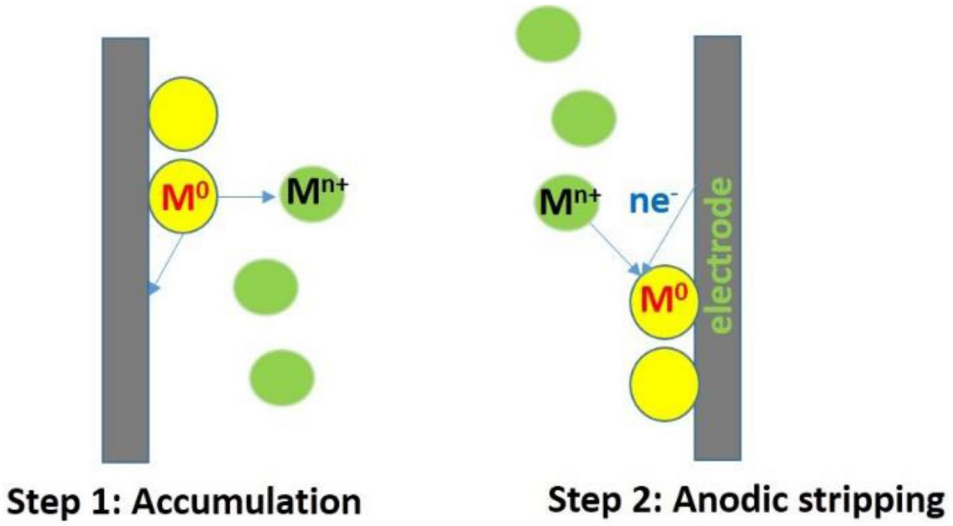

Fig. 4 Schematic representation of the mechanism of ASV approach

Recent developments of CNs for electrochemical sensing application

The nano-forms of carbon have been in lime light ever since the arrival of nanotechnology and discovery of fullerenes in 1985. Carbon nanostructures such as CNTs, graphene, and carbon nanoparticles were largely synthesized and studied due to their peculiar electrical, magnetic, and optical features. Their biocompatibility good electrical conductivity, high chemical stability, mechanical power, and surface-to-volume ratio are exceptional features which have led researchers to further explore other carbon nanomaterials [93–97]. The ability of carbon atoms to bind together in different ways have yielded several carbon allotropes with different functional characteristics [93–97] and different dimensions such as 0D, 1D, and 2D. Fullerene [98] was the first nanostructured carbon discovered followed by 1D CNTs discovered by Iijima (1991) [99]. CNTs are primarily categorized into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs comprise sp^2 carbon-forming cylindrical tubes and MWCNTs comprise rolling-up single/multiple layers of graphene [100]. The most explored 2D allotrope of nanostructured carbon is graphene. Graphene was first separated and analyzed in 2004 by Geim and Novoselov, though it was discovered and identified years ago [101]. Characteristics such as small size (usually less than 10 nm), ease of preparation, nontoxic nature, biocompatibility, good chemical stability, and good solubility [102] of zero-dimensional CNs(0D-CN) have led to an increase in studies on these materials over the last few years. Cayuela et al. proposed that nanomaterials based on 0D carbon can be categorized into three [103]: (1) carbon nanodots (CNDs), which are amorphous and quasi-spherical and do not show any quantum confinement effect; (2) CQDs, which are crystalline and demonstrate the quantum confinement effect; and (3) GQDs, which are single-sheet CNDs and p-conjugated. The excellent optical and electronic properties of these CNs have shown a great potential for various applications, ranging from energy storage and conversion (fuel cells, batteries, supercapacitors, and so on) to electrochemical sensors [104–106]. It has been possible to design flexible CNs with distinctive properties for electrochemical sensor applications [73]. Herein, we highlight the very recent developments in CN=based electrochemical sensors, particularly those based on graphene, CNTs, CQDs, and GQDs for the detection of heavy metals using voltammetry method.

Carbon nanotubes and graphene are the most widely used CNs for electrochemical sensing. CNT-based electrochemical sensors detect electroactive species involved in chemical reactions and make use of the charge transfer from solid or liquid samples to electrodes or vice versa. Several studies have confirmed the robust electrocatalytic activity of CNTs [107], and the past few decades have witnessed rapid development of CNTs and CNT-composite electrode materials for effective sensing of diverse heavy metals with improved sensitivity and selectivity [108]. A report on ultrasensitive voltammetric sensing of Cd^{2+} and Pb^{2+} using nanoelectrode arrays (NEAs) based on low-site density CNTs was made by Liu et al. wherein the NEAs were prepared by sticking an adhesive passive layer on the walls of CNTs that decreases the leakage of current and removes the electrode capacitance resulting in low background current and hence large signal-to-noise ratio. The CNTs–NEAs layered with a film of bismuth have been effectively used for voltammetric sensing of Cd^{2+} and Pb^{2+}. The LOD was 0.04 μg L^{-1} under optimal experimental conditions [109]. Nitrogen-doped carbon nanotubes (N-CNTs) were prepared by post-treatment of oxidized carbon nanotubes (O-CNTs) in the presence of NH_3 at 200, 400, and 600 °C by Joshi et al. Their role in

sensing HMIs (Cd, Pb, and Cu metal ions) using SWSV technique was investigated and it was seen that the sensitivity was better in the N-CNTs prepared at 600 °C. For real-time sensing, electrochemical detection of Cd and Pb metal ions in tap water and groundwater was investigated using N-CNTs treated at 600 °C and modified with glass carbon electrode (GCE) [110]. Qin et al. reported the use of hybrid composites of N-doped carbon spheres (N-CSs)/MWCNTs to develop improved electrodes for specific and sensitive Cu^{2+} detection by differential pulse anodic voltammetry stripping (DPASV) (Fig. 5). The suggested electrode showed a superior linear dynamic range of 0.5–200 µg L^{-1} with an LOD of 0.092 µg L^{-1} under optimized laboratory conditions [111].

A Multi-Wall CNT-modified glassy carbon electrode (GCE) was first developed by Wu et al. in 2003 for simultaneous detection of minute amounts of $Pb^{2+}$and $Cd^{2+}$by ASV. The lowest detectable concentrations of Pb^{2+} and Cd^{2+}were found to be 4×10^{-9} and 6×10^{-9} M, respectively. The stripping peak currents ranged from 2×10^{-8} to 1×10^{-5} M for Pb^{2+} and from 2.5×10^{-8} to 1×10^{-5} M for Cd^{2+} [112]. Yu et al. reported the O_2-plasma-oxidized MWCNT-altered GCE useful for Pb^{2+} and Cd^{2+} exposure by SWASV. The results indicate electrode sensitivity of 18.2 A/M for $Cd^{2+}$and 3.55 A/M for Pb^{2+}. The LOD for Cd^{2+} and Pb^{2+} was found to be 0.086 and 0.057 nM, respectively [113]. 3D porous nanocomposite comprising of graphitic carbon nitride nanosheet and oxidized MWCNTs could be used to modify screen-printed electrodes (SPE) in CV, EIS, and DPV. These modified SPEs exhibited good sensitivity and selectivity toward simultaneous identification of Cd^{2+}, Hg^{2+}, Pb^{2+}, and Zn^{2+} and under optimized conditions, the LOD at S/N = 3 varied from 8 to 60 ng L^{-1} [114].

An electrochemical sensor device based on GCE modified with polyaniline, ZrO_2-SO_4^{2-} and MWCNT nanostructures for the detection of Cr^{4+} ions was developed by Motaghedifard et al. Cyclic voltammetric studies with bare as well as PANI@ZrO_2.SO_4^{2-}@MWCNT nanocomposite modified electrode showed a much faster electroreduction of Cr4 + for the latter with an LOD of 64.3nmolL^{-1}. The studies indicate use of the system for effective sensing of Cr^{4+} ions in water released from barium chromate production lines [115]. A study by Bashir et al. using a CNT-functionalized $CoMn_2O_4$nanocomposite showed it to be an effective sensor

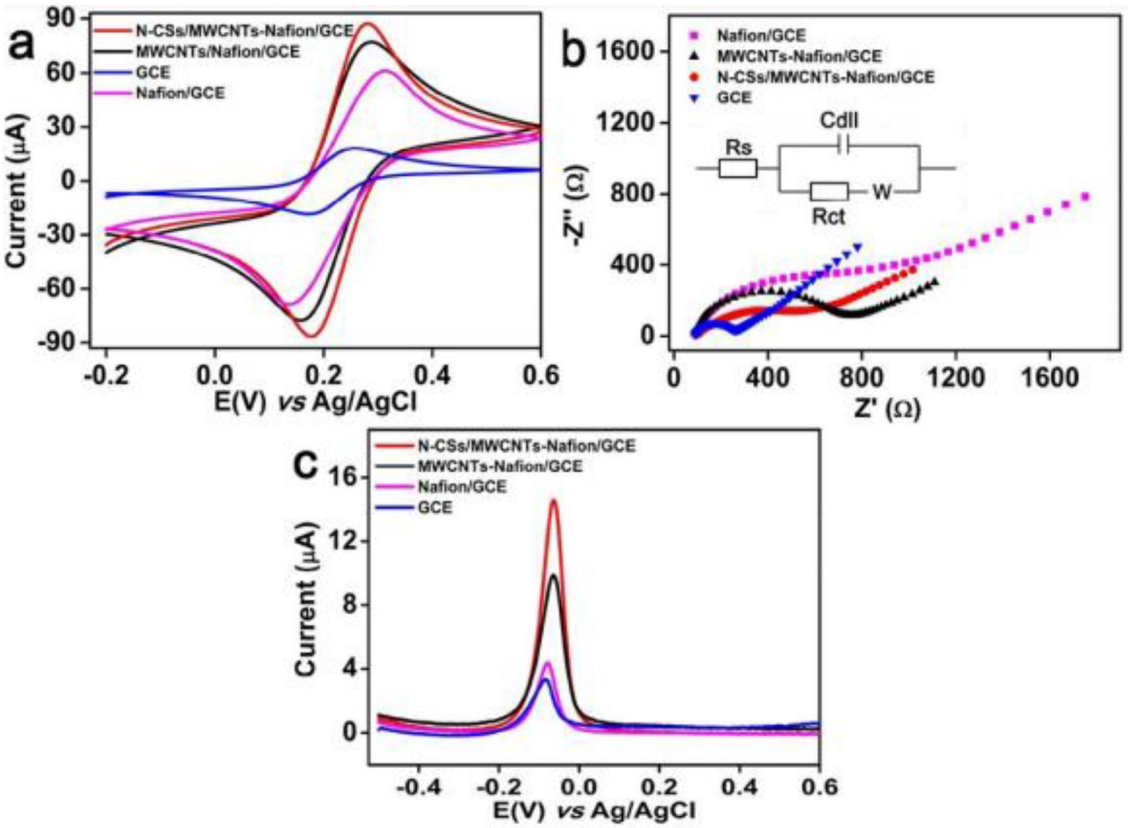

Fig. 5 **a** CV curves and **b** EIS of different electrodes in 0.1 mol/L KCl solution containing 5 mmol/L $K_4[FeCN_6]/K_3[FeCN_6](1:1)$. **c** DPASV plots of different electrodes in acetate buffer (0.1 mol L^{-1}, pH = 5.5) with 50 µg L^{-1} Cu ($^{2+}$). Preconcentration potential – 1.2 V, preconcentration time 240 s, amplitude 50 mV, period 50 ms, increment 8 mV. [adapted from reference 112 © 2019 with permission from Elsevier]

for the sensing of Pb^{2+}. The stripping behavior of the electrode was probed by SWASV and was found to exhibit excellent sensitivity and selectivity with a linear relationship between current response and Pb^{2+} concentrations from 0.01 to 0.85 µM at an LOD of 0.004 µM [116].

Graphene (2D) which consists of a single layer of carbon atoms with sp^2 hybridization [117, 118] has a high conductivity, large specific surface region, very low electronic noise, negligible fouling, and fast heterogeneous rate of electron transfer due to zero band gap [119]. These exceptional features have led to it becoming the most favorable sensing material for detecting HMIs. Reduced graphene oxide (rGO) and graphene oxide (GO) are also used as modifying materials for electrochemical sensors in view of their high specific surface area and high chemical stability. GO is usually produced from a low-priced graphite precursor using the modified Hummer process. It can be uniformly dispersed in solution furnishing plenty of electroactive sites from the oxygen functional groups present. However, GO alone cannot be used to modify the electrode since it is poorly conducting, rGO on the other hand has high electrical conductivity due to regeneration of conductive carbon-conjugated complexes. Further, grafting of nanostructures on graphene prevents its aggregation and provides nanomaterials with promising qualities. The use of graphene-based nanocomposites for the detection of HMIs has been reported [120–125] and in most of these composites, graphene or graphene derivatives have been combined with three types of material, viz., polymers [126–129], noble metals [130–132], and metal oxides [133, 134]. These include graphene/noble metal, heteroatom-doped graphene or GO, nanocomposites of graphene/metal oxides, and polymer-enhanced graphene nanocomposites. Graphene-noble metal nanoparticle composites are particularly active in the electrochemical detection of HMIs, and the most often used ones are those based on Au NPs due to their excellent chemical stability and ease of preparation [135, 136].

A study by Liu et al. reported the use of a composite film of electro-reduced graphene oxide (ERGO)-gold nanoparticles (AuNPs) for the detection of As^{3+} by ASV. The ASV current peak was linear with As^{3+} concentration ranging from 0.01 to 5 M with a sensitivity of 12.2 A/M and an LOD of 2.7 nM at optimum experimental conditions [137]. The use of Ag NPs for modification of graphene and its sensing potential have also been investigated. A study by Sang et al. describes AgNP-decorated reduced graphene oxide (AgNPs/RGO) deposited on a magnetic GCE-as an electrochemical sensor for the detection of Pb^{2+}, Cd^{2+}, Cu^{2+}, and Hg^{2+}. The sensitivities for Pb^{2+}, Cd^{2+}, Cu^{2+}, and Hg^{2+} were found to be 48.69, 40.06, 15.66, and 43.18 µA μM^{-1}, respectively with corresponding LOD values of 0.141, 0.254, 0.178, and 0.285 µM, respectively. The AgNP/RGO nanocomposite showed a considerably greater activity for anodic stripping analysis of HMIs (Pb^{2+}, Cd^{2+}, Cu^{2+}, and Hg^{2+}) compared to the simple RGO film with the overall current increase around 1.5 times greater for Pb^{2+} [138]. AgNP-loaded GO was synthesized by the ascorbic acid assisted reduction of Ag(I) on GO and subsequent stabilization with cyclodextrin. The SWASV outcomes showed that AgNP/GO/GCE determination of As^{3+} provided a higher electrochemical signal with a sensitivity of 180.5 mA/mM and LOD of 0.24 nM [139]. SWASV studies on a platinum-graphene nanocomposite-modified GCE effective in detecting toxic arsenic ion showed a narrow linear detection range (10–100 nM) and an LOD of 1.1 nM. The electrode also exhibited a fair selectivity [140] since on exposure to other

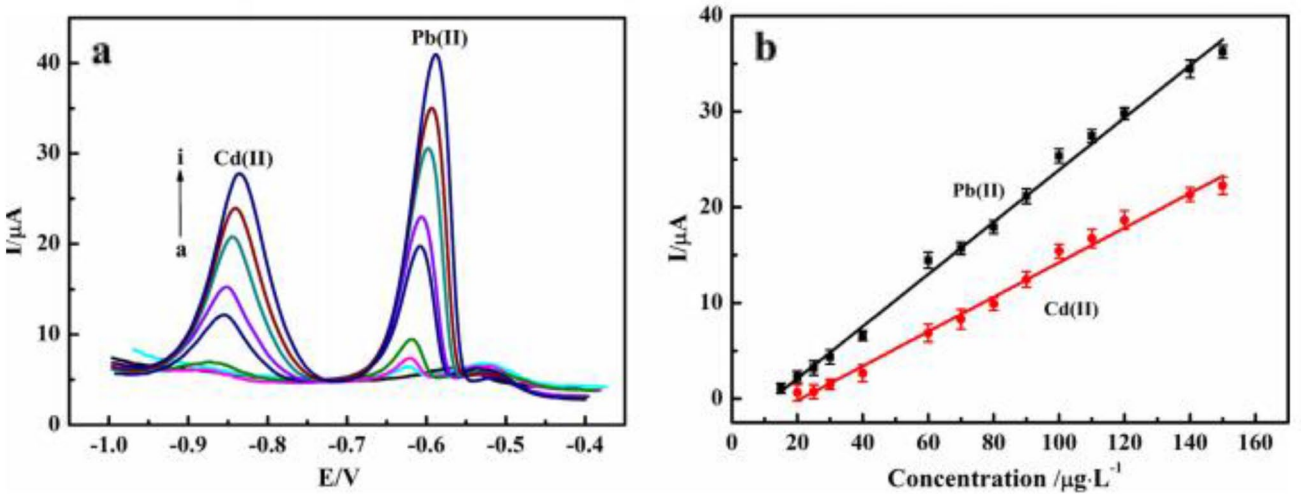

Fig. 6 **a** Electrochemical output and **b** related calibration graphs of the modified PA/PPy/GO electrode at various concentrations (from a to i 5, 15, 20, 30, 60, 80, 100, 120, 150 $\mu g L^{-1}$) toward Cd^{2+} and Pb^{2+} [adapted from reference 152 © 2016 with permission from Elsevier.]

HMIs (< 100 mM) the signal on account of As^{3+} was not disturbed. When compared to the Au and Ag nanoparticles, metal oxides possess the advantages of low cost and low toxicity and are used in HMI detection in conjunction with graphene or its derivatives. The high surface area and electrocatalytic properties of metal oxides also contribute to their greater use in HMI detection. Metal oxides with low conductivity and low stability, however, limits the electrode stability owing to the lower rate of electron transfer in the sensing process. Graphene nanocomposites based on Fe_3O_4, ZnO, Fe_2O_3, SnO_2, and TiO_2 have been successfully used to detect HMIs in aqueous solution [141–144]. A graphene-Zn nanorod-based electrochemical sensor was found suitable for the simultaneous determination of Cd^{2+} and Pb^{2+}. SWASV probes revealed LOD of $Cd^{2+}$and $Pb^{2+}$to be 0.6 and 0.8 mg L^{-1}, respectively [145]. Using thermal decomposition process, Lee et al. developed a GCE employing Fe_2O_3/graphene nanocomposites and bismuth film (Fe_2O_3/G/Bi) which could be used for simultaneous detection of small concentrations of Zn^{2+}, Cd^{2+}, and Pb^{2+}. The advantage of using bismuth film is that it creates a highly sensitive melting alloy of heavy metals. For Zn^{2+}, Cd^{2+}, and Pb^{2+}, the lower detection limits were 0.11, 0.08, and 0.07 µg L^{-1}, respectively [146]. The effect of metal oxide–rGO ratio on the sensing efficiency was studied by Vajedi et al. in the detection of Cd^{2+}, Pb^{2+}, and Cu^{2+} using CV and square-wave ASV real-time sensing techniques. The results showed 1:1 mass ratio of TiO_2: rGO acting as an effective adsorbent for Cd^{2+}, Pb^{2+}, and Cu^{2+} from aqueous solutions [147].

The use of polymers in the preparation of nanocomposites for use in electrochemical sensing is in view of the large number of functional groups on polymers. Polymer–graphene combinations offer a robust support for electrochemical sensor improvement and the possibility of different functional groups possible on the polymer afford selectivity and as well inhibit aggregation of graphene [148]. A graphene oxide–polypyrrole (pGO/PPy)-based porous electrochemical sensor developed by Song et al. for detection of Cd^2 was found to be significantly sensitive to the ion with a lower detection limit of 0.05 µg L^{-1} within the linear range of 1–100 µg L^{-1}, two orders lesser than the WHO standard limit [149]. An amyloid oligomer–rGO composite SWASV-based electrochemical sensor for the detection of Cd^{2+} and Pb^{2+}exhibited an LOD of 86.0 and 9.5 nM for Cd^{2+} and Pb^{2+}, respectively [150]. Phytic acid functionalization of polypyrrole and its use as component of the GO nanocomposite resulted in increased electrochemical conductivity with a notable surge in the peak current [151]. The modified electrode (PA/PPy/GO electrode) functioned as an electrochemical sensor for Cd^{2+} and Pb^{2+} by DPV (Fig. 6).

A similar study by Hanif et al. on glycine functionalized reduced graphene oxide/ polyaniline showed it to be an effective electrochemical sensor for fast detection of Cd^{2+} and Pb^{2+} in trace amounts with exceptional recovery percentages (102% for Cd^{2+} and 105% for Pb^{2+}) and a fair sensitivity of 41.3 µA μM^{-1} cm^{-2} for Pb^{2+} and 36 µA μM^{-1} cm^{-2} for Cd^{2+}. The LOD was found to be 0.07 nM for Cd^{2+} and 0.072 nM for Pb^{2+}. [152]. By using Au-Bi bimetallic

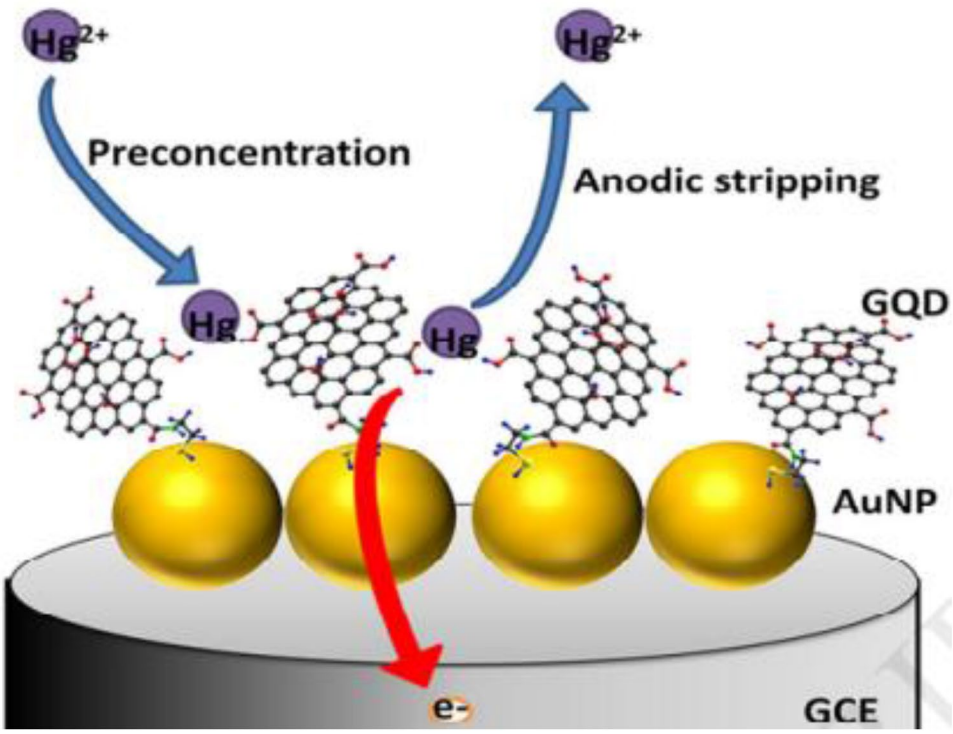

Fig. 7 Schematic illustration of Hg^{2+} detection [Adapted from reference 165 Copyright © 2015 Elsevier Ltd with permission from Elsevier]

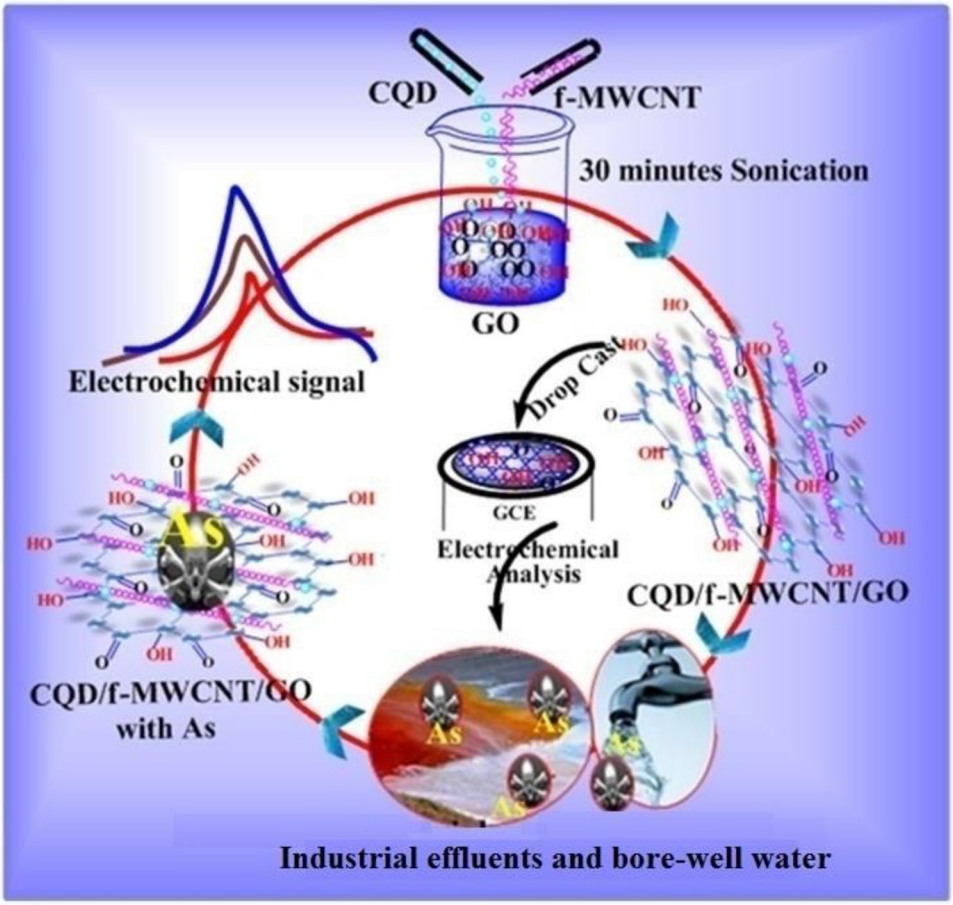

Fig. 8 CQDs/f-MWCNTs/GO synthesis and schematic representation of DPV sensing of As ion using CQDs/f-MWCNT/sGO [adapted from reference 169]

nanoparticles supported on rGO (rGO/Au-Bi) Wang and his co-workers were able to demonstrate an enhanced selectivity in the detection of Cd^{2+} and Pb^{2+}. The DPASV studies under optimized conditions (pH 4.5, deposition potential − 1.0 V, deposition time 200 s) gave response currents in good linearity with the concentration of Pb^{2+} (0.1–500 µg L^{-1}) and Cd^{2+} (0.1–300 µg L^{-1}) and lower detection limits of 0.05 µM for Pb^{2+} and 0.02 µM for Cd^{2+}, respectively [153].

Carbon dots (CDs), a relatively recent entrant to the carbon nanomaterial family, are considered to be zero-dimensional (0D) nanomaterials. Discovered in 2004 by Xu et al., CDs exhibit strong optical and electrical characteristics analogous to quantum dots owing to their quantum confinement and size effects. Quasi-spherical carbon dots composed of amorphous to nanocrystalline nuclei with diameters below 10 nm are typically referred to as CQDs and can be derived from multiple types of precursors of carbon materials. The presence of abundant oxygen-containing functional groups on the faces of CQDs makes them suitable candidates for electrochemical sensors in particular. Although CQDs exhibit good catalytic efficiency and have abundant functional groups on the surface, their conductivity is very low and overcome this problem, nanocomposites with CQDs have been considered. CDs made from graphene-based materials resemble small parts of graphene with lateral sizes below 20 nm and consisting of single, double, and multiple (< 5) layers [148, 154–160] are referred to as GQDs. The role of CDs in electrochemical sensing of heavy metal ions have been established through works of several research groups. An ASV electrochemical sensor-based N-doped carbon quantum dots-graphene oxide hybrid (NCQDs-GO) for the simultaneous detection of Cd^{2+} and Pb^{2+} reported by Li et al. gives a strong response to the ions through a linear range of 11.24–11,241 µg L^{-1} for $Cd^{2+}$and 20.72–10,360 µg L^{-1} for Pb^{2+} with LODs of 7.45 µg L^{-1} for Cd^{2+} and 1.17 µg L^{-1} for Pb^{2+} [161]. A cheap and eco-friendly electrode based on a GCE enhanced with GQDs and Nafion (NF) using SWASV was developed by Pizarro et al. for real-time determination of Cd^{2+} and Pb^{2+} in seafood. Under optimal experimental conditions results in the linear range of 20–200 µg L^{-1} with an LOD of 11.30 µg L^{-1} for $Cd^{2+}$and 8.49 µg L^{-1} for Pb^{2+} was obtained [162]. Screen-printed carbon electrode (SPCE) modified with CD could successfully detect Fe^{3+}in aqueous solution. The sensor strip showed a broad linear detection spectrum of 0.5–25.0 ppm with an LOD of 0.44 ± 0.04 ppm at a ratio of S/N = 3 under improved experimental conditions [163]. Sensors for Hg^{2+} and Cu^{2+}using GQD/AuNP composites reported by Ting

Table 2 Latest progress in carbon-based nanomaterial electrochemical sensor

Materials	Technique	Target	Linear range (μg L^{-1})	LOD (μg L^{-1})	Ref
Fe_3O_4/MWCNTs/LSG/CS/GCE	SWASV	Cd^{2+}	1–200	0.100	170
		Pb^{2+}		0.070	
MWCNT-EBP NA/GCE	SWASV	Cd^{2+}	1.0–50.0	0.060	171
$(BiO)_2CO_3$@ SWCNT	SWASV	Cd^{2+}	0–60	0.030	172
		Pb^{2+}		0.050	
Polyfurfural film/MWCNTs/GCE	DPASV	Cd^{2+}	0.5–15	0.030	173
		Pb^{2+}	0.1–15	0.010	
		Cu^{2+}	0.1–12	0.060	
		Hg^{2+}	1.5–12	0.100	
GCE-MWCNT/poly (PCV)	ASV	Cd^{2+}	1.0–300.0	0.200	174
		Pb^{2+}	1.0–200.0	0.400	
SbNP-MWCNT	SWAdSV	Pb^{2+}	–	0.650	175
		Cd^{2+}		0.770	
Graphene/MWCNT	ASV	Pb^{2+}	0.5–30	0.200	176
Graphene/polyaniline/polystyrene nanoporous fiber-modified SPE	SWASV	Pb^{2+}	10–500	3.300	177
		Cd^{2+}		4.430	
rGO-Fe_3O_4/SPE	DPASV	As^{3+}	2–300	0.100	178
Bi/MGF-Nafion/GCE	DPASV	Cd^{2+}	2–70	0.500	179
		Pb^{2+}	0.5–110	0.100	
Solvothermal-assisted reduced graphene oxide	SWASV	Cd^{2+}	1.0–120.0	1.000	180
		Pb^{2+}		0.400	
Bi-BTC/rGO	DPASV	Pb^{2+}	0.062 to 20.72	0.021	181
Fe_2O_3/Bi_2O_3 nanocomposites/ GCE	SWV	Cd^{2+}	-	0.080	182
		Pb^{2+}	-	0.070	
Bi/CP/GCE	SWASV	Cd^{2+}	50–500	25.000	183
		Pb^{2+}	25–500	10.000	
Au/rGO CNT/Bi	SWASV	Cd^{2+}	0.02–0.2	0.006	184
		Pb^{2+}		0.002	
Sb_2O_3/MWCNTs	ASV	Cd^{2+}	0.08–0.15	0.017	185
		Pb^{2+}	0.005–0.035	0.006	

LSG laser-scribed graphene; *CS* chitosan; *GCE* glassy carbon electrode; *EBP* emeraldine base polyaniline; *NA* Nafion; *SPE* screen-printed electrodes; *poly(PCV)* poly(pyrocatechol violet; *BTC* 1,3,5-benzenetricarboxylic acid; *SWAdSV* square-wave adsorptive stripping voltammetry, Bi/carboxyphenyl-modified glassy carbon electrode (Bi/CP/GCE)

et al. [164] for SWASV showed a good sensitivity of about 2.47 μA/nM for Hg^{2+} and 3.69 μA/nM for Cu^{2+} with LOD of 0.02 nM for Hg^{2+} and 0.05 nM for Cu^{2+}. The schematic representation of $Hg.^{2+}$ detection is shown in Fig. 7

Ahour et al. have described a simple yet stable and selective SWASV electrochemical sensor using GQD-modified pencil graphite electrode for the successful detection of Cu^{2+} in nanomolar concentration with a strong linearity for Cu^{2+} in the 50 ppm—4 nM concentration range and an LOD of about 12 ppm [165]. An N-doped GQD-modified N-doped carbon nanofiber (NGQDs@NCNFs) composite-based electrochemical sensor was reported by Li et al. for highly sensitive nitrite detection. CV and EIS were used to study the electrocatalytic behavior of the NGQDs@NCNFs composite. In contrast to previously reported nitrite sensors, this sensor displayed strong responses with a good linear relationship between peak currents and amount of nitrite in the range of 5–300 and 400–3000 μM with an LOD of 3 μM under optimized conditions. In addition, it exhibited good reproducibility, good selectivity, and excellent testing retrievals for sensing of nitrite present in pickle, lake water, and tap water. The results suggest the use of NGQDs@NCNF composite as a suitable material for the manufacture of electrochemical sensors [166]. Sensing Hg^{2+} in aqueous solution using indium tin oxide (ITO)-coated glass electrodes was reported by Fu et al., wherein on the basis of the studies he observed that both reduction and oxidation peak currents along with the equivalent series resistances showed a decline with increased Hg^{2+} concentration. The LOD of N-doped GQD/ITO electrodes for sensing Hg^{2+}

ions touched 10 ppb with the accumulation time of 32 s suggesting the use of functionalized GQDs in sensors for detection of toxic Hg^{2+} ions with excellent sensitivity and selectivity [167]. The sensing of arsenic, another pollutant heavy metal ion could also be carried out with electrodes modified with nanocomposites comprising of CQDs, functionalized multi-walled carbon nanotubes (f-MWCNTs), and GO [168]. The study describes improving the surface area of 3D nanostructures via grafting f-MWCNTs (1D) on GO (2D) and decorating the surfaces with CQDs, which leads to improved electrochemical selectivity, sensitivity, and renewability. CV and DPV studies showed a linear response range (0.1–11 nM) and LOD (500 pM) (Fig. 8).

Table 2 shows some recent developments in CN electrochemical sensors, especially CNTs, GQDs, and CQDs and their nanocomposites, using the voltammetry approach to detect heavy metals.

Conclusions and outlook

In the present-day scenario where detection of toxic heavy metal ions is particularly important carbon nanostructures appear to be potential candidates for the fabrication of highly sensitive electrochemical sensors in view of their characteristics such as sensitivity, electrocatalytic activity, and excellent conductivity. Herein, this review broad picture of the physical and chemical aspects of various electrochemical sensing platforms for sensing HMIs has been presented. Our review emphasizes on the application of various CNs in electrochemical systems for sensing toxic HMIs, particularly in voltammetric techniques. A drawback of the usual electrochemical systems for the detection of HMIs is the reduced reproducibility and stability, and studies have suggested the importance of developing sensors that operate in buffer solutions or simulated conditions. Hence, an understanding of the basics and application potentials of carbon nanostructures is quite necessary and will definitely lead the research to developing electrochemical sensors for environmental applications. Optimizing the performance of existing sensor schemes, including sensitivity, selectivity, and stability, is also very important. In addition, an attempt has to be made to describe the development of portable electrochemical sensors for sensing HMIs in actual samples.

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Declarations

Conflict of interest The authors declare that there is no conflict of interest regarding the publication of this paper.

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