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Rationally engineered nanosensors: A novel strategy for the detection of heavy metal ions in the environment

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ABSTRACT

Heavy metal ions (HMIs) have been mainly originated from natural and anthropogenic agents. It has become one of biggest societal issues due to their recognized accumulative and toxic effects in the environment as well as biological media. Key measures are required to reduce the risks posed by toxic metal pollutants existing in the environment. The increased research activities of HMIs detection, and use of technologies based on electrochemical detection that combine with engineered nanomaterials, is a key promising and innovative strategy that can potentially confine heavy metal poisoning. Deep understanding of the characteristics of the physicochemical properties of nanomaterials is highly required. It is also important to interpret the parameters at the nano-bio interface level that merely affect cross-interactions between nanomaterials and HMIs. Therefore, the authors outlined the state-of-the-art techniques that used engineeringly developed

nanomaterials to detect HMIs in the environment. The possible novel applications of extensive and relatively low-cost HMIs monitoring and detection are discussed on the basis of these strengths. Finally, it is concluded by providing gist on acquaintance with facts in the present-day scenario along with highlighting areas to explore the strategies to overcome the current limitations for practical applications is useful in further generations of nano-world.

Keywords: Environment; Heavy metal ions; Electrochemical detection; Nanostructured Electrodes; NanoBioModified Electrodes

1. Introduction

It has come to the limelight that certain metals such as manganese, iron, zinc and copper in the accurate proportion hold significance to life [1]. However, lesser exposure to these vital metals causes critical health and environmental hazards. On the contrary excess exposure of these metals lead to poisonous effects [2]. The reason behind this partly lies in the fact that heavy metals hold a great tendency to generate complexes mainly with different biological ligands, which contain oxygen, sulphur and nitrogen. Consequently, it can cause enzyme inhibition or breakage of hydrogen bonds and changes the protein molecular structure [3-4]. These interactions are highly reactive; hence, can be carcinogenic and toxic to both the human and the environment. The direct impact of these toxic heavy metal ions (HMIs) has been seen on the human health such as the ions of Cu, Cd, Hg, Pb (kidney or liver); Hg, Pb, As (central nervous system) and Ni, Cu, Cd, Cr (skin, bones or teeth) [5].

Being non-biodegradable, HMI exist since centuries, and they are released into the environmental ecosystem. They mainly enter into the estuarine, lake or marine sediments, leading to their introduction in the food chain system and indefinitely accumulated in predators at the top most of the food chain to higher level of environmental pollution [6].

HMIs can further make head way from one environmental area to another, which complicates the containment and treatment process [7]. The United States Environmental Protection Agency (USEPA) as well as the World Health Organisation (WHO)has established the permissible or acceptable limits for contamination of drinking water [8-9] and the values are given in **Table 1**.

A direct relation has been observed between the environmental deterioration and the quality of human life and thus making headlines globally. Consequently, environmental control of heavy metals holds immense impact for both the ecosystem evaluations and the protection of public health. To escalate control points for early warning pollution alarms, an impending requirement for real-time, in situ and immensely responsive sensors have come up, which help to specify the permissible limits of HMI refer to drinking water.

Table 1. Permissible limits of HMI refer to drinking water and their sources.

Toxic metal ions	Common sources of contamination	Scientific toxicity limits WHO (mgL^{-1})	EPA (mgL^{-1})	References
Mercury ions	Fish consumption, Environmental pollution, Industrial and agricultural operations, Dental amalgams	0.001	0.002	[10]11][8]
Cadmium ions	Metal industries, Paints, Synthetic rubber, Pigments, Electroplated parts,Smoking, Eating contaminated food	0.003	0.005	[8][12-13]
Arsenic	Volcanic eruptions, soil erosion, insecticides, wood preservatives	0.010	0.010	[8][14]
Lead	fossil fuels burning, jewellery, paint, dust, agriculture	0.010	0.015	[8][15]
Chromium	Metal processing, stainless steel welding, chrome pigment production	0.050	0.050	[8][16]
Nickel	Smoking tobacco, Industrialisation, pigments,	0.070	0.040	[8][17]

There is a significant demand for the progression of sophisticated analytical techniques for HMI detection in the parts-per-trillion and parts-per-quadrillion (ppt and ppq) range. Therefore, ceaseless efforts are made to develop trace heavy metal sensing techniques for contamination detection of different environments counting living organisms and the entire ecosystem at a new level. The notable analytical modus operandi delineated for HMI determination comprise inductance connected plasma emission spectrometry [18-19];

absorption spectrometry [20-21], mass spectrometry [22-23]; cold vapour atomic fluorescence spectroscopy [24-25]. Additionally, several other methods and techniques have been widely preferred to detect the trace or very low quantities of HMIs. These reported techniques for detection include (but not limited to) X-ray Fluorescence [26]; potentiometric methods [27]; and neutron amplification [28]. However, the above stated techniques have key drawbacks such as requirements of expensive materials, low throughput, specialized personnel to carry out the operational processes, multi-step sample preparation and excessive time consumption [29-31]. Apart from this, a significant rise in contamination of samples is seen during sample handling and storage that can lead to sample modification [32]. These collective limitations with the existing detection techniques need to be overcome by replacing with novel techniques. Subsequently, continuous attempts are being made to overcome these limitations by different researchers to develop low cost, simple, in-situ applications as well as miniature and automated measurements for the detection of heavy metal samples with minutest adjustments [33-34].

Different electroanalytical techniques have proved to be viable for replacing traditional tools for qualitative as well as quantitative analysis [35]. Simplified instrumentation, miniaturization, high sensitivity, selectivity, user acceptance, portability, least sample pre-treatment and quick processing time make them distinctive [31,34-35]. The benefits of electroanalytical approaches make the application easy and straightforward. Despite the unique properties and the advantages in processability, the industrial applications were still not victorious due to low sensitivity and limit of detection (LOD) [38]. Some analytical approaches are associated very closely, that are more relevant and reliable in selective and sensitive detection of HMIs. Sometimes, due to presence of other heavy metals (usually present in mixed media), interference in the signal of the analytical target is usually observed [39].

These problems were quite strenuous to fathom till nanotechnology sanctioned materials design model shifted from the conventional materials. Thus, the progress in the field of nanotechnology in the last few years has offered innovative tools and techniques for designing the electrode materials on the nanoscale. Nanostructures have provided the right set of circumstances to design excellent electrodes to comprehend as well as confront the limitations of existing nanomaterials. The pioneering study of noble metal nanoparticles (MNPs) [40], magnetic nanoparticles or nanocomposites [41] quantum dots (QDs) [42], and nanotubes [43] is an exciting and fascinating area of research involving the use of nanomaterials to design or modify electrodes. It has the potential to overcome all the problems associated with it so far. Based on advanced nano-characterization techniques, a profound apprehension of these nanostructured electrode materials has been obtained.

This review is primarily focused on the benefits of evolution and coalition of novel tailored macro and nanostructured materials for detection of heavy metals. The prospective applications of novel nanomaterials and possible barriers in delivering their practical implementations are discussed. The review is therefore intended to establish a compendium essence of potential future opportunities for the development of more reliable system and devices for the ultrasensitive detection of HMIs in real-samples. Hence, it runs-through the past and present-day findings as well as presents the analysis of prospects for heavy metals detection.

2. Electrode materials as a potential podium for heavy metal ions detection

Since last 15 years, significant technological efforts have been made that provide us tools required to come up with the latest techniques for regular detection and monitoring of HMI. The potential to fabricate features on solid substrates with nanoscale precision along with other characteristics such as; high sensitivity, selectivity and low price detection offers unparalleled possibilities for nanomaterials based electrochemical sensors [33]. In order to

make these technologies practically beneficial, novel electrode materials are required. Electrode materials are crucial components for the construction and development of electrochemical heavy metal sensing platforms [44]. Several electrode materials are employed for the fabrication of electrodes, and a few examples are given in **Table 2**.

Table 2. Details of electrode materials with their specific properties [45].

Electrode material	Advantages	Potential window/V	Conductivity /cm^{-1}
Indium tin oxide (ITO)	easy to process, cheaper than noble metals, stable, transparent	−0.4 - 1.9	10^4 vs 10^7
Gold	excellent conductivity, superior electron transfer kinetics, inert, easy to clean, reusability	−0.1 -1.3	10^7
Carbon	higher conductivity, quickly processed, biocompatible, Highly stable	−0.4 to 1.7	10^3
Conducting Polymers	mechanical flexibility, low cost, optical transparency, adjustable redox activity	−1.0 to 1.0	up to 10^3

Till now, a considerable variety of materials and combinations have been exhibited to be potential candidates for modification of electrodes. The electrochemical performance can be improved through the assembly of different materials. Generally, multiple factors determine the choice of material for electrochemical analysis, such as those with intensified conductivity to enhance electron transfer, the material with increased porosity and increased surface area which have an advantage of more active sites usually for metal ion binding [46]. Through customised assembly and functionalization, these engineered materials can be efficiently assembled on the surface of electrodes to provide a model sensing platform. It will also help in sensitive detection approach towards a distinctive targeted metal ion and further selective detection of HMIs [47].

Owing to the excessive applications of various types of nanomaterials, they are in trend to develop electrochemical sensors, ultimately making them a highly operational area of analytical chemistry. Therefore, this article distinguishes materials into various sections and sub-sections such as; inorganic nanomaterials, organic materials, and biomaterials, as

shown in **Figure 1**. Additionally, this article reviews the contribution of each component in electrochemical sensing of HMIs.

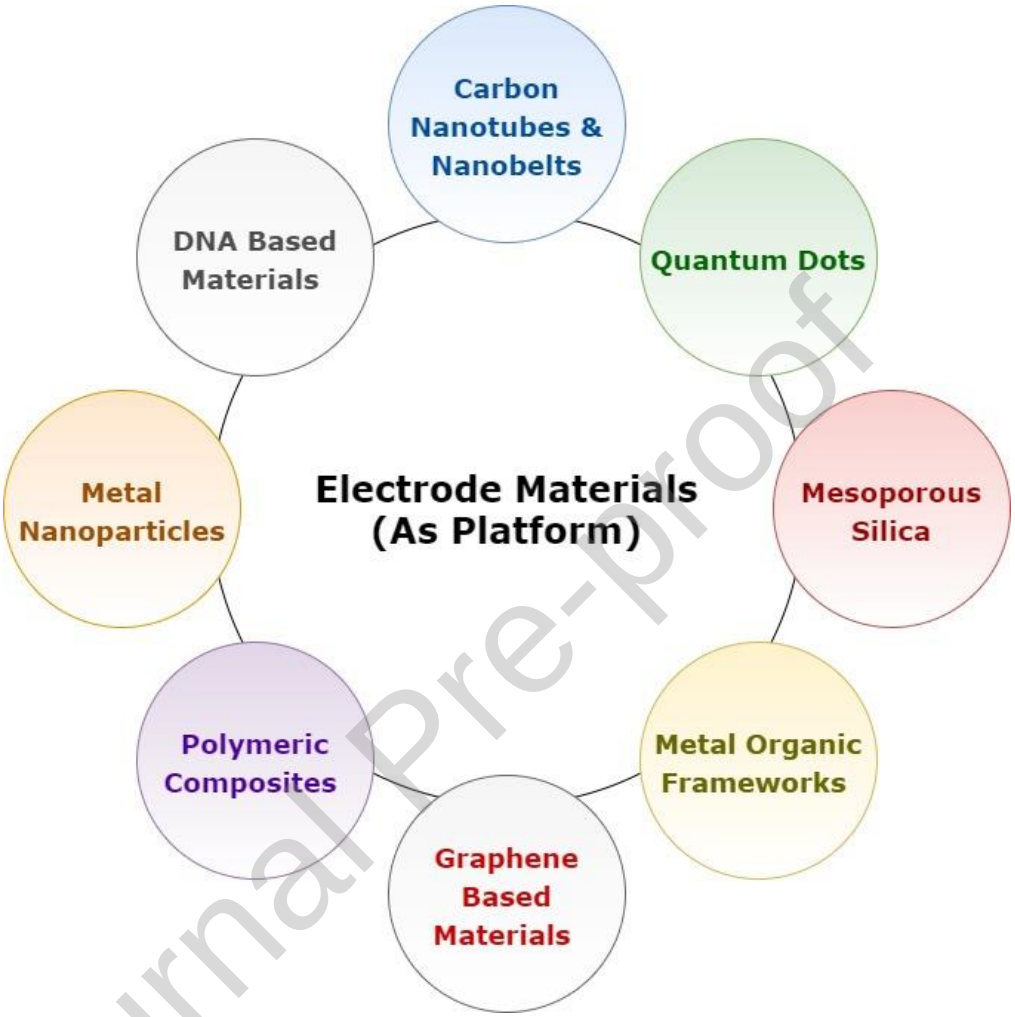

Figure 1. Various forms of electrode materials used for detecting HMIs.

The selection of precise design and development of advanced engineering based nanosensors with the best fitting and precise architecture will further help in metal ions selectivity from the matrix samples. In this context, **Table 3** summarises the latest development on engineered nanomaterials for detection of HMIs.

Table 3. Engineered nanomaterials based detection of HMIs by electrochemical techniques.

Working electrode nanomaterials	Toxic HMIs	Detection limit	Technique	Sample type	References
Metal nanoparticles					
AuNPs-GN-Cys composites	Cd^{2+}, Pb^{2+}	0.10 μg L^{-1} 0.05 μg L^{-1}	SWASV	real water sample	[48]
$MnCo_2O_4$ nanoparticles	Cd^{2+}, Pb^{2+}	7.02 nmol/dm^3; 8.06 nmol/dm^3	linear sweep anodic stripping voltammetry (LSASV)	natural waters	[49]
$MnFe_2O_4$/GO	Pb^{2+}	0.0883 μM	SWASV	real water sample	[50]
DMG-Nafion® /SPE	Ni^{2+}	0.03 mg/L	DPV	soil, ground and environmental waters	[51]
Kaolin platinum electrode (K/Pt).	Cd^{2+}	5.4×10^{-9} mol L^{-1}	SWV	natural water samples	[52]
Metal-organic frameworks					
Ln-MOF/ ZJU-27	Cd^{2+}, Pb^{2+}	1.66 Nm; 1.10 nM	SWASV	drinking water and West Lake	[53]
Cu-MOF	Hg^{2+}	0.0633 nM	DPV, CV	Tap water, Tuna Fish	[31]
Fc-NH_2-UiO-66	Cd^{2+}, Pb^{2+}, Cu^{2+}	8.5 nM, 0.6 nM, 0.8 nM	CV, EIS	Tap water	[54]
MOF UiO-66-NH_2- graphene aerogel (GA) matrix	Cd^{2+}, Pb^{2+}, Cu^{2+}, Hg^{2+}	0.02 μM, 1.5 nM, 7 nM, 2 nM	Differential pulse stripping voltammetry (DPSV)	river water and the leaching solutions of soil and vegetable	[55]
Ni-based MOF	Pb^{2+}	5.08×10^{-7} mol/L	SWASV	simulated wastewater	[56]
CNTs based					
PyTS–CNTs/Nafion® / PGE	Cd^{2+}, Pb^{2+}	0.8 μg L^{-1} ; 0.02 μg L^{-1}	DPASV	Environmental samples	[12]
MWCNTs/peptide	Cd^{2+}, Hg^{2+}	2.749 X 10^{-8} M; 9.068 X10^{-10} M	CV	Wastewater	[57]
MWCNTs/NA/Bi/SPE	Pb^{2+} Zn^{2+} Cd^{2+}	0.01 mg/L	DPASV	Water from lake, drinking, tap water	[58]
MWCNTs/Schiff base	Pb^{2+} Hg^{2+}	6.00 X 10^{-4} Mm 9.00 X10^{-4} mM	SWASV	Seawater, tobacco, marine and human teeth	[59]
L/MWCNTs/CPE(IL)	Cd^{2+}	0.070 mg/L	DPASV	Tobacco, hair, milk powder, Edible fungi	[60]
Graphene or graphene oxide based					
GO–MWCNTs	Pb^{2+}, Cd^{2+}	0.2 μg L^{-1}; 0.1 μg L^{-1}	DPASV	Water	[61]
3D graphene-framework/Bi nanoparticles	Zn^{2+}, Pb^{2+}, Cd^{2+}	300 μg/L 0.02μg/L 0.05 μg/L	EIS, SWASV	Lake water, Tap water	[62]
GO-modified Au	Pb^{2+}, Cu^{2+}, Hg^{2+}	0.4 ppb 1.2 ppb 0.8 ppb	Cyclic voltammetry		[63]

3DGO-Py10	Cd^{2+}	3.6 μg L^{-1}	SWASV	Lake water, Tap water	[64]
GO(SN-rGO)	Hg^{2+}	8.93 nM	SWASV	natural water	[65]
Quantum dots/ Mesoporous Silica/ Polymeric/ DNA based					
Graphene quantum dots (GQDs)-AuNPs	Hg^{2+} Cu^{2+}	0.02 nM 0.05 nM	ASV		[66]
Nanoporous silica	Hg^{2+}	7.0×10^{-8} M	Ion-selective electrode (ISE)	wastewater and fish samples.	[67]
Polysulfoaminoanthraquinone (PSA)	Pb^{2+}	1.6×10^{-7} M	ISE	Saliva, tap water, tea leaves, and river water. F	[68]
AuNPs-glutathione (GSH)/cysteine	Hg^{2+}	50 pM	DPV, EIS	Wastewater samples	[69]
Exo III Metal Ions reshuffling on Thymine-Rich DNA duplexes	Hg^{2+}	0.2 nM	DPV	-	[70]
rGO/CMC/GSH/GCE	Cd^{2+}	0.05 nM	CV, EIS	Egg albumin (EA) and milk.	[71]
Microelectrode arrays based detection					
Au-microelectrode array	As^{3+}	0.0212 ppb	ASV	Water	[72]
Bismuth film microelectrodes	Pb^{2+}	2.2×10^{-8} mol/L	ASV	-	[73]
Au- gel integrated microelectrode arrays	As^{3+}	1nM	SWASV	fresh and marine aquatic systems	[74]
bi-band silver microelectrode (b-BAgmE)	Pb^{2+}	0.4 nmol·L^{-1}	CV, EIS	water	[75]
Au microelectrode/MB-tagged DNA	Hg^{2+}	0.02 μg L^{-1}	SWV	water and fish	[76]
Microfluidic electrochemical devices					
Bismuth	Pb^{2+}, Cd^{2+}	8 ppb, 9.3 ppb	SWASV	cell culture media soil pore water ground water	[77]
Carbon	Pb^{2+}, Cd^{2+}	2ppb and 2.3 ppb	SWASV	contaminated aqueous samples	[78]
bismuth plated on carbon	Pb^{2+}	1 ppb	SWASV	-	[79]

3. Electrochemical sensing techniques for detection of HMIs through inorganic nanomaterials

Owing to the significantly higher performance characteristics, excellent progress has been observd in recent years into the synthesis and deterministic assembly of improved inorganic nanostructured material categories. The most widely accepted nanomaterials include carbon-based nanomaterials, *i.e.* graphene and graphene oxide, carbon nanotubes (CNTs), metal or metal oxide-based nanomaterials, porous-coordinated metal-organic frameworks and their related materials. In addition to this, few other nanobiomaterials like polymers and DNA based nanomaterials have widely been preferred by different researchers for the detection of HMIs.

3.1. Metal nanoparticle modified electrode

Because of unique physicochemical properties, metal oxide and metal nanoparticles have been the first line of options for electrode production and HMIs detection. Sensing via metal nanoparticles is advantageous due to the bulk properties such as; comparatively quick electron transfer rate and enhanced electrode surface area. Compared to the traditional macro electrodes, the nanomodified electrodes possess relatively high mass sensitivity, declined effect of solution resistance, escalated mass transport rate, and elevated signal to noise ratio [71-72]. In combination with anodic stripping voltammetry, antimony and bismuth, these nanoparticles have proved remarkably reliable and sensitive for heavy metal trace analysis.

The unique behaviour of nanomodified electrodes based on antimony and bismuth is mainly due to the development of multi-component alloys and their improved sensitivity. It is mainly due to the combination of superior characteristics of noble nanostructured materials [82]. Lee and colleagues [83] introduced a sensitive and user friendly electrode in an electrochemical sensor for trace analysis of HMIs. They synthsised and characterised the Bi nanopowder by levitational gas condensation (LGC) process for detection of HMIs. A TEM image of Bi developed nanoparticles, spherical in shape, revealed quality performance for HMI detection. The LOD for concurrent endurance of Pb and Cd have been measured and reported circa 0.07 and 0.15 µg/L, respectively. It was mainly established for proceeding the signal-to-noise features of the reaction intended for the 1.0 µg/L solution reaction after completion of 10 mins of accumulation. Gold-based nanoparticles (AuNPs) modified electrodes have also shown to be an adaptable analytical method for the detection of HMIs. It is mainly because of their immense surface functionalities [5,84]. An ultrasonic Hg(II) sensor was demonstrated by Gong *et al*., [85] by

making use of a nanocomposite film composed of graphene and monodispersed AuNPs as the potential podium. The uniform and homogenous distribution of AuNPs onto the graphene nanosheet matrix led to the construction of a monodispersed AuNPs-based ensemble, which highly facilitated the sensing behaviour and electron-transfer for Hg (II) detection that caused notably enhanced selectivity and sensitivity. The detection limit was considerably low, *i.e.* 6 ppt, which is very low as per the guideline values of WHO.

Wan *et al*. [86] reported a sensitive and simultaneous detection of copper lead by electrochemical method. It was based on commercial screen printed gold electrode (SPGE) which was modified by gold nano particles (GNPs). The dynamic surface area reported to be amplified by 1.65 epochs by the sulfuric activation. The SPGE was subsequently used to modify with GNPs and the sensitivity was reported to be 0.154 A/ppb as well as 0.084 A/ppb for lead along with copper respectively.The value coefficient of correlation (r^2) was reported to be 0.9792 and 0.9896. The findings of the results showed an improved resistance for interference, more enhanced reproducibility, and more comprehensive detection range between 20-300 ppb.

Bimetallic alloys with core-shell structure is extensively used as electrochemical sensing platform for the detection of different concentrations of HMIs. Owing to the existence of optical, catalytic and magnetic features, it is better than the single metallic component. Renedo and co-workers reported [87] anavant-grade electrochemical analytical technique designed for the explicit detection of antimony(III) and sulfide(III) and analysis was performed by anodic stripping voltammetry technique. They carried out the experimental work by amending screen-printed electrodes by silver nanoparticles (AgNPs). LOD for Sb (III) was obtained using modified electrodes of silver and gold, and reported to be 6.79 X 10^{-10} M. The reproducibility, repeatibility, precision or exactness using above-stated method was given in terms of % relative standard deviation (RSD) values. It was estimated

to be 3.50%. Similary, Gong *et al.*, reported [88] the applicational advantages of bimetallic nanoparticles of Au-Pt NPs. GCE was modified by inorganic-organic based hybrid nanocomposites for selective and ultrasensitive detection of Hg^{2+}. The nano-hybrid of Au-PtNPs/NF modified on electrode has been reported to have substantially enhanced selectivity and sensitivity for Hg(II) stripping assay. The LOD has been reported to be very low, *i.e.* 0.008 ppb.

Due to exceptionally appealing and attractive catalytic, nano-morphological, non-toxic, efficient functional biocompatible properties of nanoparticles of metal-oxides such as Fe_3O_4, NiO, ZnO, SnO_2, ZrO_4, TiO_2, MnO_2 and MgO, they have been extensively used for detection of HMIs [89].

In 2010, Liu *et al*. [90] designed and developed DNA-based steeply allied conductive carbon hybridized TiO_2 nanotubes (DNA/C-TiO_2 NTs) arrays for efficient, ultrasensitive and discerning the exposure of lead (Pb) ion in an environmental sample. The newly developed electrochemical sensor provided a broad linearity range of calibration from 0.01 to 160 nM with picomole level LOD at 3.3 pM. AuNPs have recently been developed for sensing of As(III) by electrochemical technique. While designing and developing a sensor, GCE was modified with newly synthesised AuNPs. Detection was carried out by CV technique in a wide potential window range of 400 to 1100 mV. It was carried out for 10 cycles. The evaluation and detection of As (III) by the developed sensor was carried out in a real water sample. The GCE modified with AuNPs resulted in more improved redox potentials as compared to the bare electrodes. The recognition bound reported to be 0.28 ppb through high sensitivity. The newly developed electrochemical sensor was found to be robust, stable and interference-free [91].

3.2. Metal-organic frameworks (MOFs)

Novel MOFs are widely accepted electrode materials for sensitive and selective detection by electrochemical techniques. They are largely recognised as promoting electrode modifiers based on the high porosity, the larger surface to volume ratio and tuneable space for coordination [92]. Because of the exceptional durability and stability (hydrothermal and chemical) of zeolitic imidazolate frameworks (ZIFs), they are known for the modification of electrodes and electrochemical detection [93]. Zhang et al., [94] synthesised and characterised core-shell matrix based nanostructured materials with high sensitivity and selectivity for trace amount of HMIs detection in real water sample. Newly synthesised and characterised nanostructured material mainly consist of an Fe(III) dependent metal-organic system (Fe-MOFs) along with mesoporous nanocapsules of Fe_3O_4@C nomenclature reprented as Fe-MOF@mFe_3O_4@mC. It exhibited higher dispersion behaviour in aqueous solution with enhanced bio-affinity and higher porosity. Therefore, it can be proposed as a possible material for the electrodes with high electrochemical activities. The results exhibited higher sensitivity in broader linearity range from 0.01 to 10.0 nM. The reported LOD for sensitive detection was found to be 6.73 and 2.27 pM towards As^{3+} and Pb^{2+}, respectively. Further, Zhang and co-workers [95] synthesised and characterized novel MOFs based nanomaterials for concurrent revealing of copper(II) as well as lead(II) by electrochemical technique. They functionalized MOFs by incorporating phytic acid and polypyrrole. The obtained MOFs was nomenclatured as PA/PPy/ZIF-8@ZIF-67. The simultaneous detection has also been well demonstrated for copper(II) as well as lead(II) by electrochemical technique. The obtained LOD was reported to be 14.8 and 2.9 nM, respectively. The performance and efficancy of the newly modified electrode was reported to be of excellent and superior quality and the performance excellence was attributed to the outstanding electrical conductivity of PPy, the larger surface area of ZIF8@ZIF-67, and the

metal complexation power of PA. Recently, a novel electrochemical sensing system for mercury (Hg^{2+}) ion detection in tap water and canned tuna fish was reported by Singh *et al*. [31] They put forward Cu-MOF based nanoparticles exhibiting unique large surface area being favourable for the absorption of Hg^{2+} and preconcentration. The LOD was found to be very good, i.e. 0.0633 nM. The linearity range was reported to be 0.1–50 nM for Hg^{2+}.

3.3. Carbon Nanotubes

Carbon-based materials exhibit tremendous potential as electrode materials in electrochemistry. The advantadge of carbon materials includes easy processing, abundance, low cost, high chemical stability, non-toxicity, higher specific surface area, wide opening temperature range and good electrical conductivity [96]. Carbon holds the capability to create various low-dimensional nanostructures with significant mechanical, electronic, optical and thermal properties. Above stated features make carbon nanomaterials peculiarly captivating for next-generation electrode materials [97]. Innumerable efforts have been made for exploring the sensing potential of carbon nanotubes (CNTs) towards HMIs detection as given in **Table 2**.

CNTs are cylindrical nanostructured allotropes of carbon with remarkable physicochemical properties. They offer comparatively larger surface area with higher electrical conductivity and mechanical strength. This makes them ideal in the materials science research, electronics and in the nanotechnology domains [98][44]. Bagheri et al., [99] synthesised novel nanocomposite composed of triphenylphosphine and ionic acid MWCNTs. It was synthesised for sensitive, selective, and real-time simultaneous revealing of Hg(II), Cd(II) and Pb(II). Square wave anodic stripping voltammetry (SWASV) technique was successfully employed to examine the electrochemical reaction and characteristics features of the modified electrode towards analyte's ions. The experimental conditions were designed to ensure the simultaneous determination of HMIs in real sample.

An intensified electro-chemical sensing performance was observed in newly synthesised material in comparison to the existing conventional carbon-paste based electrodes. It has been widely practiced for concurrent determination and recognition of Pb^{2+}, Hg^{2+} and $Cd^{2+,}$ in real sample. The successful usage was mainly attributed to the application of ionic liquid as the substantial binder designed for CNTs. The responses of the modified electrode for Hg^{2+}, Cd^{2+} and Pb^{2+} detection was improved as compared to the ones obtained by the use of conventional carbon paste electrode. He *et al*., [100] synthesised multifunctional novel nanocomposites of $Zn_3(PO_4)_2$@DNA and $Zn_3(PO_4)_2$@MWCNT-DNA. They were established on $Zn_3(PO_4)_2$. It was comprised of Hg^{2+} beset DNA strands and multi-walled CNTs (MWCNTs) along through immobilised Hg^{2+} targeted DNA strands. The electrochemical impedance spectroscopy (EIS) technique was used to recognise practiced intended for the recognition of HMIs. The detection mechanism was based on the development and improvement of T-Hg(II)-T, proper organisation among Hg(II) ions and DNA imparts. It offers featured benefits of the high amount of adsorption of Hg (II) emerged from hollow nanostructure of $Zn_3(PO_4)_2$. Selective and sensitive detection of Hg (II) were observed due to immobilized T-rich DNA strands. The developed nanomaterials resulted in high LOD of 0.071 nMin in the range of 0.1–50 nM. Wu *et al*., [101] reported the concurrent recognition technique for zinc (II), mercury (II),cadmium (II), copper (II) and lead(II) by voltammetric technique. For this, they modified GCE with nanoparticles of magnetite (Fe_3O_4) as well as fluorinated multiwalled carbon nanotubes (Fe_3O_4/F-MWCNTs). The newly synthesized nanomaterials resulted in an improved and increased detection efficiency primarily due to uniform dispersion of Fe_3O_4 and presence of MWCNTs or F-MWCNTs in nanocomposites. The sensitivity of Fe_3O_4/F-MWCNTs was considerably higher than Fe_3O_4/MWCNTs, or Fe_3O_4. A marvellous agreement was recorded between the low-cost Fe_3O_4/FMWCNTs sensor and classic techniques coupled with atomic

fluorescence spectrometry or plasma mass spectrometry) in soybean samples and river water. This Fe_3O_4/F-MWCNTs sensor has shown phenomenal performance in terms of reliability, selectivity, stability and replicability.

3.4. Graphene or graphene oxide

Being a classical two-dimensional material (2DM), graphene possesses a sheet-like faveolated structure that has been employed in both primary and applied researches [102]. It has an excellent and magnificent characteristics such as ultrahigh electron mobility, large surface area, and outstanding thermal conductivity. These exemplary features support the wider use of graphene in the fabrication of hybrid materials for development of different electrochemical sensors [29]. The significant benefits of graphene or its derivatives are the capability of surface treatment to be a good host for immobilizing other nanoparticles. Also, this attribute has been used to boost the signal and to enhance the sensitivity of metal ion sensors. Since long, sensors based on graphene have been immensely and extensively used for the detection of HMIs [103]. Furthermore, graphene is more widely accepted in the electrochemistry detection due to declined usage of GO. It mainly consist of different functional groups like carboxyl and hydroxyl, which form complexes with HMIs [104]. It will draw attention to significant applications of electrochemical sensors of graphene nanocomposites and graphene for HMI, as shown in **Figure 2.**

The film-based synthesised nanomaterials of Nafion®–graphene (Nafion® -G) composition was used in development of electrochemical sensor. The developed electrochemical sensor not only possessed improved sensitivity for metal ions detection of Cd^{2+} and Pb^{2+} but also helped in minimising the interferences owing to the synergistic effects of Nafion® and nanosheets of graphene [105]. This dramatically increased the stripping current signal on graphene electrodes. The combinational effects of improved rGO

electron conduction and cationic-exchange property of Nafion® is the reason for increased sensitivity [106,107].

For most of the HMIs detection, a nanocomposite based on Tin oxide (SnO_2) was synthesised and evaluated. The SnO_2 and reduced GO was used to develop SnO_2/rGO composite. This nanocomposite was also used in modification and fabrication of electrode for the electrochemical detection. Moreover, it was utilized for selective, sensitive as well as simultaneous detection of various HMIs like Hg(II), Pb(II), Cd(II) and Cu(II) in drinking water. LOD remained notably lower than the estimated WHO guideline value. While, SWASV electrochemical technique was used to detect HMIs [108].

A new, advanced photoelectrochemical electrochemical sensor was designed by Foo and co-workers [109]. It was centred on the viable binding affinity of cadmium sulfide (CdS) and Cu^{2+} on the surface of electrode. Another electrode based on CdS/rGO/CC has been recentlydeveloped on pliable carbon cloth (CC) substrate through nanoparticles of CdS and reduced graphene oxide (rGO). By utilising the metal sulphide forming mechanism, a delicate and discerning photoelectrochemical technique was developed to perceive a trace expanse of Cu^{2+}. The electrochemical detection mechanism was mainly established on the reasonable binding affinity amid CdS-Cu^{2+}. The criteria for selection of synthesised composite materials with graphene-based materials was the crucial parameter for the electrode fabrication, sensing efficiency and performance. Further, nanomaterials of polyglycine-modified graphene paste electrode (PGMGPE) was used for ultrasensitive detection of Pb^{2+} and Hg^{2+}through cyclic voltammetry (CV). The modification on the electrode surface with newly synthesised materials enhanced the performance and behaviour of electrodes for selective and sensitive revealing of HMIs. The output of the current peak resulted into linear range variation with increase in concentration. It resulted in good recognition bound of 6.6 and 0.8 μM of (Hg(II)) and (Pb(II)), correspondingly [110].

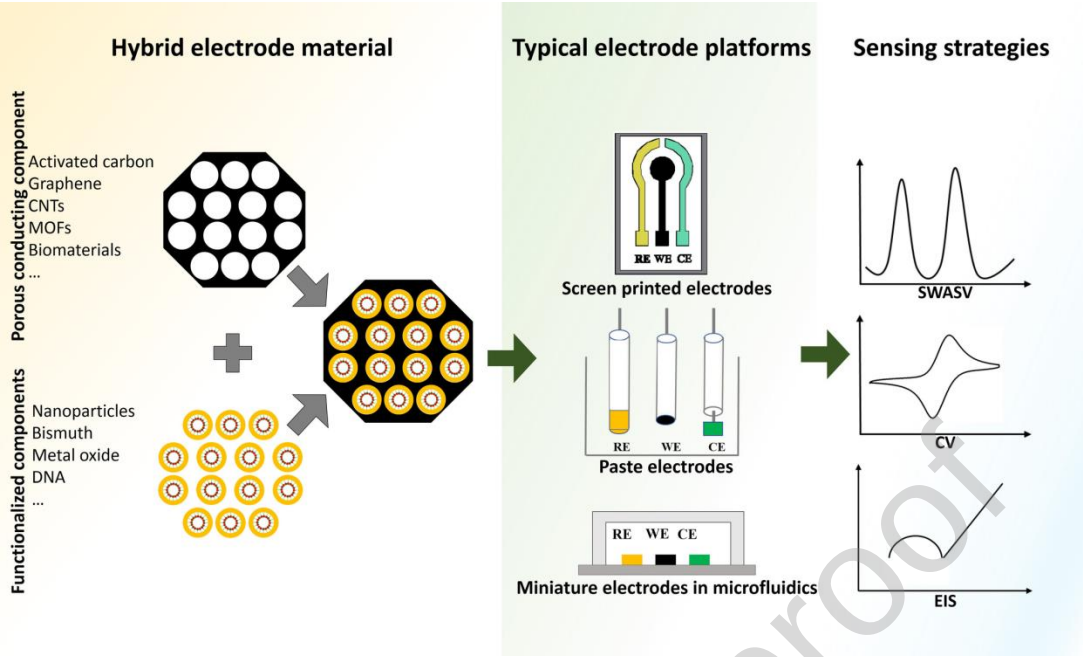

Figure 2. Hybrid electrodes composed of porous, conductive and high-end materials [46].

3.5. Quantum dots (QDs)

Quantum dots are a powerful method for detecting biological interactions by tracking changes in the properties of light emission. The distinctive features such as physical robustness, size-dependent emission energies, small size and flexible surface functionalization have accumulated outstanding attentiveness for HMI detection [111]. QDs may also be optimized to a broad range of ultraviolet (UV) to near-infrared (NIR) emissions owing to their quantum extent influence. They are indeed better than the traditional organic fluorescent dyes, photostable substances with widespread excitation but narrow Gaussian emissions [112]. Vázquez-González et al., discussed the existing literature on QD established sensors designed for the utmost pertinent toxic HMI, Cd^{2+}, $Hg^{2+}$and Pb^{2+} (in different configurations) [113].

Duan et al. [114] instigated a new environment friendly fluorescence sensor for Hg^{2+} ions focused on N-acetyl-l-cysteine (NAC)-capped ZnS QDs in aqueous solution. Quantitative detection of Hg^{2+} remain advanced centred on fluorescence quenching with strong selectivity and specificity. Under the optimized experimental condition, LOD was

reported to be 5.0×10^{-9} mol L^{-1} without any interference. As per Wang and co-workers [115], QDs depicted fluorescence quenching outcome once explored through Hg^{2+} and CdTe. Usually, CdSe QDs are designed for the detection of Hg^{2+}. Analysis results and recognition showed that quantum yield of synthesized CdTe remained relatively small, that restricted the extensive exploration. They claimed that based on the electron transfer mechanism, Hg^{2+}could constructively quench NIR-emitting QDs. The applications in the real sample was performed and Hg^{2+} level in milk power and HeLa cells with adequate outcomes was detected. The LOD of the sensor was measured to be 10^{-9} M. However, QD-based sensor is not generally appropriate due to toxicity associated with QDs.

3.6. Mesoporous silica

Owing to controllable pore size, greater surface area and small pore-size distributions, HMS, MCM-48, MCM-41 and SBA-15 mesoporous silica are highly regarded in electrochemical detection applications. Their sensitivity to target metals can be improved by adding appropriate functional groups onto the surface [116]. Sacara et al. [117] used four types of ordered mesoporous silica powders (MCM-41 and SBA-15) and amino-functional mesoporous silica (MCM-41-NH_2 and SBA-15-NH_2) to detect Cd(II). They modified GCE coated with ion-exchange polymer Nafion®. SVASV technique was used for detection. The influence of pH and silica for proceeding the reaction of the electrodes was also considered. The consequence of amino-functional groups grafted to Cd(II) ion detection on the silica surface was also studied. The detection limits for Cd(II) were reported between 0.36 -1.68 μM with the current silica-modified electrodes.

Cotolan et al. [118] have developed a modern lead ion detection technique using silica-modified GCEs in several biological and environmental samples. The changed electrodes with four diverse illustrations of ordered mesoporous silica (OMS) powders were demonstrated by using SWASV technique. Strong analytical parameters in a well-defined

oxidation peak between -0.5 V vs Ag/AgCl/KCl_{sat} emphasised the reliability of the prepared electrodes and the high peak current at either bare or the OMS modified GCE.

3.7. Nano biomodified electrodes for electrochemical sensing of HMI

Combining nanomaterials with the unique complexing characteristics of the receptors contributes to the detection of HMIs with enhanced sensitivity and excellent selectivity for stripping analysis in an advanced electrochemical sensing network. Nanobiomodified based materials can be primarily categorized into; a) polymer-based materials and b) DNA based materials [46]. The literature compendium of nano bio-modified electrodes for electrochemical sensing of HMIs is given in **Table 3.**

Pan *et al.*, [119] modified GCE nanomaterials/ionophore-modified for anodic disrobing detection of lead (Pb^{2+}). Nano-sized hydroxyapatite (NHAP) has a distinctive three-dimensional complex organization. It has powerful adsorption ability towards Pb^{2+}. Lead ionophore improves the electrochemical platform's susceptibility and selectivity designed for this metal. The electrode has an undeviating array of approximately 5.0 - 0.8 μM through an open-circuit potential amassing epoch of 10 mins.The sensitivity and detection bound of the suggested sensor was measured to be 1.0 nM. An electrochemical sensor was developed by Wang *et al*. [120] especially for detecting cadmium ion. They synthesised UiO-66-NH_2@PANI by polymerizing the conductive polymer polyaniline (PANI) round the MOFs UiO-66-NH_2. The detection was reported to be linear for Cd^{2+}in the concentration range of 0.5–600 μg L^{-1} with the continuous repeatable results. Under the optimized conditions, the lowest LOD was reported to be 0.3 μg L^{-1}. Almost similar work has been reported by Kong *et al*., [121] for trace detection of Cd^{2+} and Pb^{2+}. Core-shell ferric oxide@polyaniline (Fe_3O_4@PANI) nanoparticles were developed. The primed electrochemical sensor showed enhanced sensitivity, excellent specificity and stability with LOD of 0.03 and 0.3 nmol L^{-1} for Pb^{2+} and Cd^{2+}, respectively.

DNA based biosensors emerged to be encouraging in the detection of heavy metals due to the fact that DNA and DNAzymes are biodegradable, extremely choosy, facile to procure using the in-vitro technique with additive advantage of portable analytical device. Apart from this, electrochemical recognition of specific analytes provides direct electronic signals which conquers the usage of high-priced signal transforming tools [122–124]. Nowadays, electrochemical biosensors based detection of HMIs is focused on modifications of GCE by DNA and nanomaterials [125].

Recently, many researchers described the detection of Hg^{2+} by DNA and nanomaterials. Kong *et al.*, [126] in 2009 developed an exceptionally selective and sensitive electrochemical biosensor for ultrasensitive detection of Hg^{2+} in aqueous solution. The findings were designated on the basis of the specific, stable and accurate attachment of Hg^{2+} by two DNA thymine bases (T–Hg^{2+}–T). They used AuNPs-functionalized DNA for signal amplification. Three elements developed the electrochemical mercury biosensor. The first element was 5'thiol-modified oligonucleotide which contained six T-bases for Hg^{2+} binding mainly as a capture probe denoted as DNA 1. The second component was a suitable oligonucleotide linker denoted as DNA 2 through the 30-terminal corresponding through the capture probe sequence excluding for six T-T mismatches. The last one was AuNPs functionalized with DNA 3, which could precisely hyberdize near the 50-terminal with the partial linker chain. With AuNP-functionalized DNA amplification, Hg^{2+} could accomplish a detection limit of 0.5 nM. It enables the detector suitable for Hg^{2+}assays in very low concentration into the real samples. But the main drawback with this system is higher detection limits and reusability problem. Slocik et al. [127] have investigated 2-aminopurine-modified DNA homopolymers for detecting mercury and silver. The newly developed sensor consisted of AuNPs functionalized with a specific peptide ligand.

Both the free 2AP base and 2AP interaction were entrenched through DNA homopolymers and metal ions amplified the signal. Poly-T and poly-C DNA have respectively increased the Hg^{2+} and Ag^{+} signals by 14- and 10-fold. Both mercury and silver metal ions possessed LOD of 3 nM. Interaction of PFNs with metal ions outcame in a typical colorimetric reaction induced by nanoparticles accumulation. Shen and colleagues [128] described an assay technique of the DNA-Au bio barcode-based electrochemical detection of lead. The significant key benefit of DNAzyme catalytic reaction is an excellent binding affinity with Pb^{2+}. The unique architectural feature takes preferably to DNA-Au bio bar codes for signal improvement. The strands of barcodes were used as both a surrogate target and an amplification tool. The electrochemical DNAzyme biosensor centred on the extension of the DNA-Au bio bar code imparts a platform to evaluate several small molecules, notably metal ions. An electroactive complex, RuHex, which made use of an electrostatic activity to retain the ability to bind to the anionic phosphate of DNA strands behaves as a signalling transducer. The DPV technology has helped examine the electrochemical interaction and behaviour of RuHex with DNA. A redox mediator was used as an electrical signal reader for this analysis. The electrochemical sensor reveals a 1000-fold increase in detection limit as compared to colourimetric sensors. Zhou *et al.*, [129] reported a new, unlabelled, immobilised DNA-based biosensor through an well-organized, mesoporous carbon nitride (MCN) for ultrasensitive detection of Ag^{+}. They used $[Fe(CN)_6]^{4-/3-}$ as the redox couple. They reported sensitive and specific detection of Ag^{+} using electrochemical impedance spectroscopy (EIS) technique by immobilising DNA through mesoporous carbon nitride (MCN) on the electrode. Hairpin-like structure resulted after interaction between Ag+ and DNA molecules by hybridization with the probe. After interacting with Ag^{+}, it was further changed to the duplex-like configuration in solution to form a C-Ag^{+}-C complex at the

surface of the electrode. The LOD was illustrated to be 5×10^{-11} M with reasonable high specificity.

Given the fact that the device is extremely sensitive, the functional implementation is difficult. To resolve this, the technique should be closely researched, along with the avoidance of time-consuming procedures, reproducibility and robustness.

3.6. Microelectrode and nanoelectrode arrays

Microelectrode arrays (MEAs) and nanoelectrode arrays (NEAs) were extensively used in electrochemical sensing of HMIs to enhance LOD and sensitivity. In the past two decades, microelectrode arrays have also gained popularity in electrochemical analysis and sensor technology owing to their well-known benefits. They have unique electrochemical properties, low dimensions due to which they deliver limited capacitive charging currents, very high mass transport rates, very little limited ohmic drop and steady-state current diffusion [130]. In addition, microelectrodes often show high spatial resolution in chemical monitoring or in other electrochemical processes without disrupting the process [131]. Microelectrodes and nanoelectrodes have a large signal-to-noise ratio, rendering them superior to traditional macroelectrodes. Microelectrodes and nanoelectrodes are typically used to detect HMIs, because they provide greater current density, quicker mass transfer rate and lower charge transfer resistance than traditionaly available electrodes [124-125] In addition to this, there is no need to use any additional electrolytes and convection to carry out the study. Only a small current is needed for stripping analysis. On the other hand, this eliminates interference in the analysis [134].

Light-addressable potentiometric sensor (LAPS) is the most well-recognized multi-analyte sensing semiconductor. The notable features of the LAPS are complete flatness, simple and easy to fabricate on electrode surface [135]. LAPS provides the highest sensitivity, longer stability, and linearity-based detection [136]. In comparison,

development cost of the material is very economical. LAPS chips are being developed and available at reasonable rate. Hence, LAPS is also used in electrochemical analysis methods [137].

For simultaneous determination of $Cu^{2+,}$ Pb^{2+} and Hg^{2+}, Lv et al., [138] 2018 designed and developed an ultra-high sensitive microelectrode that was based on carbon nitrides. Nano frameworks formed by multi-walled carbon nanotube were first prepared on a carbon fibre disks microelectrode by an advanced drop-casting method on the functionalised oxygenous functionalized carbon nitride nanosheets. They reported the LOD was lower i.e. 1.0×10^{-13} mol L^{-1}, 1.8×10^{-11} mol L^{-1}, 8.0×10^{-12} mol L^{-1} in the linearity range of $6.6 \times 10^{-12} \sim 8.5 \times 10^{-6}$ mol L^{-1}, $8.1 \times 10^{-10} \sim 8.5 \times 10^{-6}$ mol L^{-1}, $2.2 \times 10^{-11} \sim 8.5 \times 10^{-6}$ mol L^{-1} for Cu^{2+}, Pb^{2+} and Hg^{2+} respectively.

3.7. Microfluidic electrochemical devices

Microfluidics is considered an emerging technique, in size ranging from tens of microns to hundreds of microns on a chip employing a microchannel to control or manipulate multiple microfluids [139]. The microfluidics comprises of planar substrates with depth (~10 μm), width (~100 μm) and height (10 mm), respectively [140]. Microfluidics provides multiple benefits with broad range of applications. Numerous advantages include miniaturising in size, limited solvent and reagent requirements, quick reaction times, easy detection and single chip integration of multiple sensors [141-142], which is also known as lab-on-a-chip (LOC).

Jung et al. [143] reported reusable polymer lab chip microfluidic sensor of Pb(II) ideal for mass production and low-cost analysis. The miniature chip sensor was microfabricated by cyclic olefin copolymer (COC). This was fabricated with silver as a working while silver as counter electrode and quasi-reference electrode (QRE). Additionally, SWASV was used to detect Pb(II) ions. LOD was reported to be 0.55 ppb with linearity over 1-1000

ppb. Subsequently, Rattanarat et al., [144] developed easy and inexpensive technologies for colorimetric and electrochemical detection of HMIs. Colorimetric identification for Ni, Fe, Cu, and Cr, and electrochemical detection for Pb and Cd illustrate the efficacy of this method. LOD with ASV technique was reported to be low as 0.25 ng (Cd and Pb).

4. Common additives required for the synthesis of nanomaterials

The understanding of modified electrodes has been of considerable importance intended for the progress of a novel generation of electroanalytical instruments with enhanced selectivity and sensitivity. The significant role of modifiers is to impart exciting properties to support, leading to accurate recognition and pre-concentration of the analytes. Methods for modifying a conductive surface include covalent bonding, coating with chemically synthesised materials, *e.g.*, soluble polymers, or electrodeposition, as an electro synthesized modifier. Various common additives are often practical in altering bare electrodes to expand the sensitivity, selectivity and stability**.**

Chitosan: As a natural polysaccharide, chitosan (CS) is produced by deacetylation of chitin, the most biodegradable, non-toxic and biocompatible natural amino polysaccharide [145]. With positive charges in its amine groups, the cationic biopolymer interacts with anionic molecules which constitute the principal reactive groups of metal ions [146]. Consequently, CS has been utilized for electrochemical fortitude of HMIs. These distinguishing characteristics enable CS for a extensive array of applications in the fields of food technology, cosmetics product, pharmaceutical development, sensors instrumentation and bio-sensors development [147]. To detect As(III), a coherent electrochemical sensor was constructed based on arsenic adsorption on a uniquely modified electrode. The modification of working GCE was carried out by Chitosan-$Fe(OH)_3$ complex and a reducing agent L-Cysteine. With ASV, a linear correlation of 2-100 ppb (R^2 = 0.974) with LOD 0.072 ppb was acquired [148]. Wu *et al*., [149] revealed

the adsorption of lead, copper, and cadmium ions on crosslinked chitosan-carbon nanotubes (Chit-CNTs). Using square-wave anodic stripping voltammetry, the electro-chemical behaviours of Chit-CNTs film modified GCE was labelled for distinct and concurrent recognition of $Pb^{2+,}$ Cu^{2+} and Cd^{2+} in 0.2 M, pH 5 acetic buffer solutions. For discrete recognition, the concentration sort remained 1.50–4.44 ppm. The recognition bound was reported to be 0.8 ppm for Cd^{2+} with R^2 = 0.975; 0.25–1.24 ppm through a recognition bound of 0.1 ppm (R^2 = 0.978) for Cu^{2+}; and 0.63–3.70 ppm through a recognition bound of 0.6 ppm for Pb^{2+} (R^2 = 0.972), respectively.

Nafion®:Nafion® is typical sulfonated material generally used for proton exchange membranes (PEMs). Along with this, it is a public selected design for many other electrochemical applications and can upgrade the stability of the modified layer [150]**.** Wang *et al.* [151] synthesized film of Nafion® , which was loaded with novel MWCNTs. It was used to modify a GCE electrode, using europium ion (Eu^{3+}) to identify a trace amount of metal ions. The contact between the sides of the MWCNT and the hydrophobic backbone of Nafion® enables the MWCNT to disperse in Nafion®. This formerly applied to the top of the GC electrode as a thin film. The electrochemical response to Eu^{3+} was observed to improve by 10 times in comparison to the concentrations of MWCNT in the range of 0.5 and 2 mg/mL. Under complete optimized circumstances, the level of Eu^{3+} remained resolute by Osteryoung square-wave voltammetry technique subsequently a pre-concentration period of 480s. A linear range from 1 to 100 nM was obtained through a maximum recognition bound of 0.37 nM. Palisoc *et al.* [152] modified the pencil graphite electrodes (PGEs) through nanoparticles of bismuth and Nafion® by means of a drop-coating system for precise trace detection of cadmium (Cd^{2+}) and lead (Pb^{2+}) ions as instances of too high temperature processed milk. Anodic stripping voltammetry was used

to analyse the samples with the modified PGE as the functional electrode.The detection limit was reported to be 7.31 μg/L, 31.07 μg/L for Cd^{2+} and Pb^{2+}, respectively.

Ethylenediaminetetraacetic acid (EDTA): EDTA is a unique chelating reagent capable of forming stable complexes with heavy metals and enables them to re-dissolve in water. Chelating ligands are favourable materials because they tend to form the complex with metal ions [153]. It improved the carbon paste electrode (CPE) by EDTA to detect Hg (II) ions (in the aqueous medium) using square wave voltammetry.The modified electrode proposed significantly low limit of detection (8.6×10^{-9} M after 5 min preconcentration time) with exquisite reproducibility [154]. In the same year, Deshmukh and colleagues synthesised EDTA functionalized polypyrrole (Ppy) nanocomposite for ultrasensitive detection of Pb(II) by and SWNTs. The electrochemical detection of Pb(II) ions was carried out by using EDTA-Ppy/SWNTs nanocomposite in an aqueous media. This Ppy/SWNTs nanocomposite was adapted through EDTA by making use of the dip-coating process at room temperature. The EDTA-Ppy/SWNTs adapted stainless steel electrode (SSE) displayed exceptional selectivity and sensitivity detection of Pb(II). The LOD attained for Pb(II) came out to be 0.07 μM [155].

5. Challenges and future frontiers for sensing toxic HMIs

Presently, environmental pollution caused by heavy metals is an inclusive issue. Even though the HMI concentration in the natural environment is in traces, but still they carry the tendency of accumulation in the human body to a considerable level via the food chain. With the perspective to diminish environmental pollution and alleviate the subsequent deterioration of ecosystems and its detrimental outcome on human health, it is vital to precisely regulate the heavy metals concentration. While the conventional analytical methods make it feasible to detect lower limits of analytes in the samples, but those found limited applicability for direct detection of metallic contamination in the intracellular

media. This brings immense difficulties in developing the novel electrochemical technologies for sensing heavy metal, for regular and long-term uninterrupted inspection of HMIs concentration. Appreciable research has been conducted on improving and designing HMIs detection techniques in biological and environmental media. All these desirable attributes potentiality possess a scientific challenge that needs to be dealt with. Due to the surging importance of heavy metals detection, the practice of the electrochemical techniques has exhibited the capacity to increase detection and confirm their competency over conventional analytical methods.

To answer the most stringent analytical challenges, miniaturized electrochemical techniques should be studied. Various approaches designed for recognition of HMI have been established on the latest modification of electrodes with nano or micro nanomaterials have been evolved. The nanomaterial-based electrochemical sensors for HMIs detection offer newer opportunities with benefits like rapidness, cost efficiency, high sensitivity and selectivity. To enhance the applicability of nanomaterial-based electrochemical detection, the combination of nanomaterials such as MNPs, graphene, CNTs and biological receptors were extensively used. It offers a great grade of specificity, sensitivity and selectivity. It makes the advanced sensing setups outstanding intended for the strategy and assembly of cohesive recognition schemes in existing illustration applications. The use of nanostructured constituents in the development of these sensors has contributed to an improvement in the repeatability, sensitivity and sensitivity of such sensors with a low limit of detection (range of ppt). These approaches have emerged from mere proof-of-concept studies to "platform technologies"that can be amended to detect HMIs.

In future, a lot of attention should be paid to upgrade the sensitivity and selectivity of the nanomaterials for detecting the trace amount of HMI. Till now, a little attention has been paid on the economical synthesis of high-performance nanostructured electrode materials. It

possesses enormous significance for extensive commercial applications, to investigate environmentally friendly and accessible routes for cheap large-scale synthesis of nanomaterials. It can be further recommended that interrelated strategies, such as the addition of some additives like Nafion® , EDTA etc., should be explored. Along with this, it is also proposed that the addition of newer binders and electrolyte additives will assist in enhancing the performance of electrochemical sensors using nanostructured electrode materials.

In addition, the synergy of nanomaterial properties with nanotechnology enables the significant potential for the development of extremely high integrated recognition organisations which allows dedicated online or even embedded heavy metal detectors which are relevant to environmental revisions and further allied arenas. It can be proposed that advanced miniature methodologies will pave the way for easy, economical, affordable, rapid and multiplexed HMIs detection.

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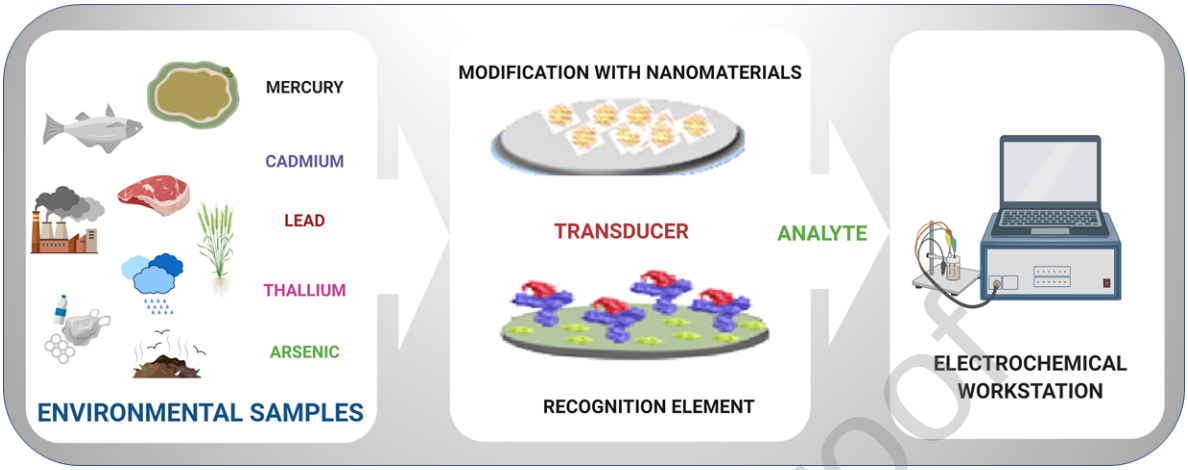
Graphical Abstract



Highlights

- Overview of nanomaterials for electrochemical detection of heavy metal ions.
- Design and deployment of new functional nanomaterials are summarized.
- Potential knowledge gaps and research needs in the heavy metal detention system.
- Prospects to design highly sensitive electrochemical sensors are proposed.

Credit Author Statement

Arshid Numan: Conceptualization. Atal A.S. Gill: Data curation, Writing - original draft. Saqib Rafique, Manisha Guduri, Yiqiang Zhan, Balaji Maddiboyina, Lijie Li: Writing - original draft, reviewing and editing. Sima Singh, Nguyen Dang Nam: Conceptualization, Supervision, Writing - review & editing.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: