# Composites Based on Conducting Polymers and Carbon Nanomaterials for Heavy Metal Ion Sensing (Review)

Megha A. Deshmukh, Mahendra D. Shirsat, Almira Ramanaviciene, and Arunas Ramanavicius

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# Composites Based on Conducting Polymers and Carbon Nanomaterials for Heavy Metal Ion Sensing (Review)

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## ABSTRACT

Current review signifies recent trends and challenges in the development of electrochemical sensors based on organic conducting polymers (OCPs), carbon nanotubes (CNTs) and their composites for the determination of trace heavy metal ions in water are reviewed. OCPs and CNTs have some suitable properties, such as good electrical, mechanical, chemical and structural properties as well as environmental stability, etc. However, some of these materials still have significant limitations toward selective and sensitive detection of trace heavy metal ions. To overcome the limitations of these individual materials, OCPs/CNTs composites were developed. Application of OCPs/CNTs composite and their novel properties for the adsorption and detection of heavy metal ions outlined and discussed in this review.

## Introduction

Heavy metal ions play a vital role in widening the spectrum of environmental pollution issues. Water sources are the foremost target of heavy metal ion contamination, and these heavy metal ions are non-degradable.[1] Heavy metal ions step-in in an environment through many pathways like mining activities, smelting, agriculture, chemical, metallurgical industries, pulp industries, waste disposal, etc. Some heavy metal ions play an essential role in the metabolic system balance of the human body, but in limited quantity. The consequence of heavy metal ions on living organisms is life risking. Pb(II), As(II), Hg(II), Cd(II) and Cu(II) are the most hazardous metal ions. Long-term exposure to metal ions can cause several health risks viz. skin problems, headache, digestive system problem, depression and cancer. It also effects on the human nervous system, kidney damage and tubular damage.[2] Gradually, all these facts are increasing the need of detection and quantification of heavy metal ions through water or air sources. For example, the maximum permissible concentration recommended by WHO in drinking water are, for Ni(II) at 0.2 mg/L, Cd(II) at 0.01 mg/L, Cr(II) at 0.1 mg/ L, Cu(II) at 2 mg/ L and Pb(II) at 0.5 mg/ L.[3]

Thus, there is an immense need of heavy metal ion sensors for detection and real-time monitoring of metal ions in water, which is essential for living organisms, the environment and to maintain a safe water supply.[4,5]

The most widely used and appreciated traditional methods for heavy metal ion analysis are atomic absorption or emission spectroscopies, inductively coupled plasma mass spectrometry, inductively coupled plasma-atomic emission spectrometry, cold vapor atomic fluorescence spectrometry, high-performance thin layer chromatography.[6,7] Some of these methods are able to analyze many metal ions simultaneously.[8] However, everyone is also aware of the limitations of these instrumental techniques such as high cost, requires more space for equipment, laborious pre-treatment processes, etc.[9] Thus, to overcome the limitations electrochemistry-based techniques applied for analytical purposes. The most reliable fact about these techniques is, utilized for sensitive and selective diagnostic applications.[10] One of the most often used electrochemical technique is amperometry, which is based on oxidation or reduction reactions on electrode surface and enables the determination of analyte in turbide solutions, which is not possible by spectroscopic techniques.[11] Certain years ago, the most often materials used for heavy metal ion detection are mercury,[12] gold and silver electrodes,[13,14,15] gold nanoparticle-modified electrodes,[16,17] bismuth film electrodes,[18,19], antimony film electrodes,[20,21] boron doped diamond electrodes,[22,23] diamond like carbon electrodes and[24,25] electrodes modified biomolecules (whole cells, peptides, DNA, enzymes, etc.).[26,27,28] Nevertheless, all these materials also have some limitations for their regular use in the determination of metal ions.

Mercury-based electrodes such as mercury film and hanging mercury drop electrodes (HMDE) are most widely used traditional electrodes for heavy metal ion sensing due to their high sensitivity toward target metal ion, reproducibility, purity of surface, amalgam formation ability, etc. However, in spite of all these excellent properties and performance, mercury has been severely restricted or banned for future regulations and occupational health consideration due to its toxicity.[29,30] Bismuth film electrode has some favorable attractive properties compared to that of mercury electrode, because it shows high sensitivity, well-defined stripping

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signals, good resolution of DPV-peaks during the determination of metal ions, wide cathodic potential range, etc.[29] However, interference is an unresolved issue with bismuth film electrodes. The major interferences such as bismuth hydroxide formation at pH 4 takes place, which leads to irreproducible measurements.[31] This affects reproducibility and mass production of sensors based on bismuth films.[32] Biomaterials considered as highly selective materials for heavy metal ion sensing, even in the simultaneous detection of more than one analytes.[1] However, the most of biomaterials are relatively unstable. In order to avoid instability gold electrodes has been used in the electrochemical detection of metal ions.[33,34,35] However, selectivity of the electrode is a crucial issue of unmodified gold electrodes. Various nanoparticles can be applied for the determination of heavy metal ions due to their high surface area, mass transport and catalysis.[36,37,38] However, rapid passivation of some nanoparticle modified electrodes is an issue due to aerial oxidation.[36,39] Therefore, diamond-based electrodes, which shows better stability, were introduced in area of electrochemical analysis,[41] because diamond has unique properties like hardness, highest atomic density, wide potential window and excellent dielectric properties.[42,43] These unique characteristics grip the attraction of researchers for the application in the determination of heavy metal ions.[44,45,46] However, the most critical problems in diamond electrodes are related to the synthesis of well-characterized structure. Therefore, these traditional materials were consequently replaced by conducting polymers and their composites with carbon nanomaterials, which have the most suitable physicochemical properties for determination of metal ions. Accordingly, day-by-day, recent era of material science widens the gamut of potential applications of these materials. Therefore, this review will be more specifically focused on application of conducting polymers and carbon nanomaterials in sensors dedicated for heavy metals.

Conducting polymers *viz.* polyaniline.[47,48] polyacetylene, polypyrrole, polythiophene, polyphenylenes grasping significant attention[49,50,51] due to their unique physical, chemical, electrical properties, good processability, environmental stability, low-cost ease of synthesis, charge transfer ability, tailoring of properties by doping etc.[52,53,54] The foremost credit of introduction of carbon-based materials goes to Ijjima, he has introduced the interesting features of carbon-based material through his report in 1991.[55] Single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) are forms of carbon-based allotropes.[56] These materials are known for advanced mechanical, electrical, chemical, thermal properties and the large surface to volume ratio.[55,56] Consequently, advanced properties of these materials are attracting researcher's desirability for diverse practical applications.

Thus, the main emphasis of this communication is to review of heavy metal ion sensors based on the conducting polymer, carbon nanotubes and carbon-nanomaterial/conducting-polymer-based composite materials and their properties.

## Carbon nanomaterials for the determination of heavy metal ions

Graphene and carbon nanotubes are the most exciting carbon nanomaterials, discovered during the last four decades. Pristine graphene, graphene oxide (GO), and reduced graphene oxide (rGO) belongs to the members of graphene family.[57] The simple and low-cost mass production of graphene through reduction of GO is also the key factor for the increased demand of graphene in material science. Thus, graphene-based materials are attractive due to their advanced features such as high specific surface areas, high electron mobilities due to zero band gap and exceptionally low electronic noise.[58,59] Therefore, graphene-based materials are fulfilling the ideal requirement such as rapid and sensitive detection in heavy metal ion sensor technology.[60,61]

Preparation of cathode using electrochemically deposited rGO on the surface of carbon felt (CF) for the removal of dye pollutants and wastewater decontamination from persistent organic pollutants has been reported.[62] The resulting cathodes offer an enhanced electrochemical properties like an increase of the redox current and decrease in the charge transfer resistance in presence of the redox probe $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$. It shows improved kinetic properties compared to pristine CF.[63] Non-covalently modified rGO-based sensor for ultrasensitive and selective detection of $Hg^{2+}$ in an aqueous phase has been reported.[64] The reported sensor has shown excellent response toward $Hg^{2+}$. The detection limit of the sensor to the analyte is 0.1 nM. The reported sensor shows superior performance due to the introduction of electrochemically reduced GO (ERGO)-based diode with N-[(1-pyrenyl-sulfonamido)-hepty l]-gluconamide (PG) as the modifier. Nafion-graphene (Nafion-G)-based composite film-based electrochemical sensors for the detection of $Pb^{2+}$ and $Cd^{2+}$ has been also reported.[65] Nafion-G based sensor shows improved sensitivity toward analytes as well as improved interference properties due to the synergistic effect of graphene nanosheets and nafion. Thus, the stripping current signals greatly boosted on graphene electrodes. The enhanced electron conduction of rGO and the cation exchange capacity of nafion show high sensitivity.[66,67]

CNTs, closely related to the structure of fullerene $C_{60}$ molecule discovered by Kroto.[68] The erection of CNTs based on elemental carbon in the sp2 hybridization. The structure of SWCNTs and MWCNTs based on number of graphene sheets, which are forming structure of nanotubes[56] as it is shown in Figure 1.

The easiest way to describe CNT structure is cutting of $C_{60}$ molecules in two halves, which can connected to the two ends of the cylindrical graphite sheet. These carbon-based materials show outstanding physical, chemical, structural, thermal
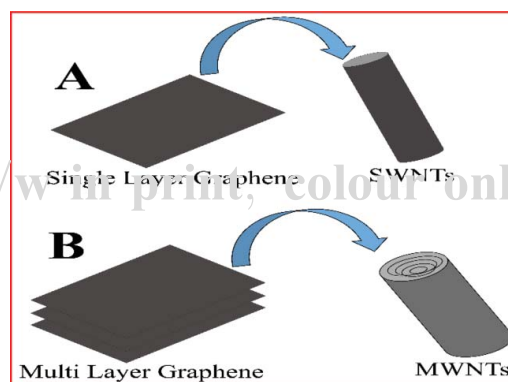


**Figure 1.** Graphene and carbon nanotubes as (a) single-walled carbon nanotube (SWCNT) (b) multi-walled carbon nanotube (MWCNT) structure.
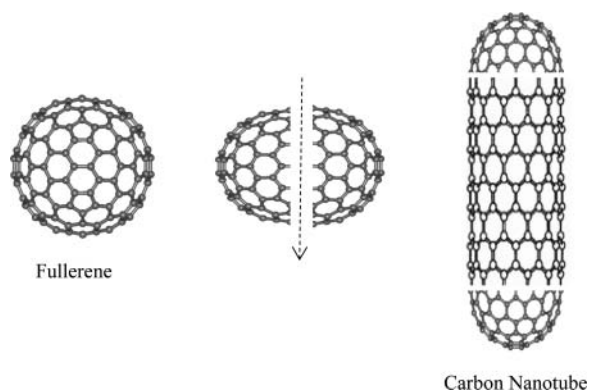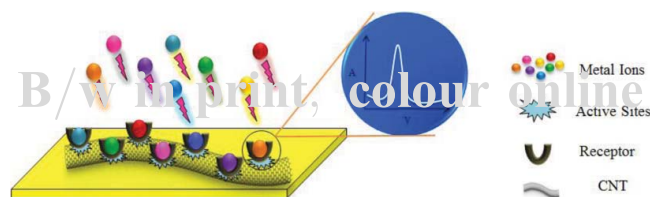
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Figure 2. Structure of carbon nanotube.



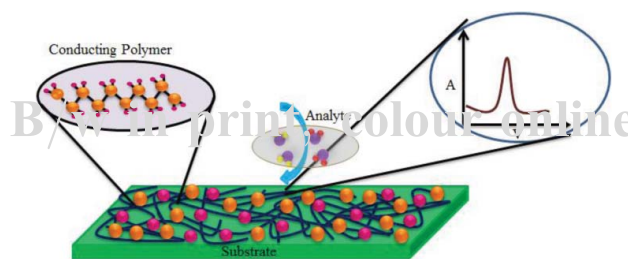Figure 3. Carbon nanotubes-based heavy metal ion sensor.



Figure 4. Schematic presentation of organic conducting polymer based heavy metal ion sensor.
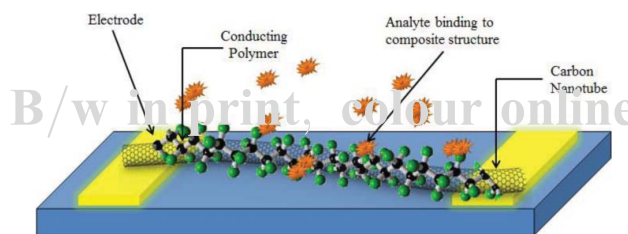


Figure 5. Heavy metal ion sensor based on carbon nanotube functionalized with organic conducing polymer.

properties, large surface to volume ratio, extraordinary stiffness, significant elasticity, etc.[69]

Carbon nanotubes show unique electrical properties, having very low resistance.[70] Remarkable stiffness and large axial strength of CNTs based on sp2 hybridization of carbon atoms, which are involved into structure of CNTs.[71] Before the invention of CNTs, diamond was the foremost thermal conductor, but CNTs shows the thermal conductivity twice of that of the diamond.[72] CNTs drew major concern in the field of detection of heavy metal ions due to their ability to form complexes with heavy metal ions.[73] High surface to volume ratio with active sites, controlled distribution of pore size, exceptional sorption capacity and high sorption proficiency make CNTs suitable material for the development of electro-analytical systems dedicated for the detection of heavy metal ions.[74,75] Under the same experimental conditions, it was observed that MWCNTs and SWCNTs show superior adsorption capability toward Ni(II), Zn(II) and Cr(II) ions. Particularly, sorption capability of CNTs is active over a broad pH range up to 7 to 10.[69] Despite of high cost, researches based on the application of CNTs more widespread compared to other carbon-based materials such as activated carbon due to their more efficient sorption/desorption properties and possible easy regeneration.[69,74] In recent years, advantageous application of CNTs in nanofilters for the reduction of contaminant concentration in wastewater has been increased.[76] The morphology of the CNTs is also an admirable key factor for their potential application in metal ion sensing.[56] Some researchers proposed that modified CNTs play important role in the metal ion sensing due to their imminent ion exchange properties. Oxidized CNTs are more capable of cation uptake compared to not oxidized CNTs.[77] Contrariwise, not oxidized CNTs have potential toward uptake of anions compared to oxidized CNTs.[78] Among these above observations, it was determined that oxidation has impact on the point of zero charges (pHPZC) of CNTs, which eventually oversees the overall surface charge.[79,80,81] Typically, oxidation of CNTs impact on $pH_{PZC}$ of CNTs thereby resulting in

predominantly negatively charged surface, which is more constructive for cation uptake. Therefore, unoxidized CNTs carry a higher $pH_{PZC}$ which results in a predominantly positively charged surface, which is more favorable for anion uptake.[56,79,80] The oxidized CNTs can play important role in uptake of cations.[56] In the case of graphene, the honeycomb structure-based 1 atom thick layered structure of graphene can be covalently attached to chemical moieties mainly via carboxyl and hydroxyl groups. Electrochemical sensors based on modified CNTs are represented in Table 1.

## Application of organic conducting polymers in sensors for the detection of heavy metal ions

Organic conducting polymers (OCPs) viz. polyaniline, polyacetylene, polypyrrole, polythiophene, polyphenylene and many others have some advanced physical, chemical and electrical properties.[105,106] OCPs also attracts the attention of the research communities due to their diverse practical applications in recent technologies viz. membranes, supercapacitors, batteries, transducers, photodiodes, sensors etc.[107] One of the most significant properties of OCPs, which make them extremely attractive material for chemical sensors are, sensitivity to minor electrochemical perturbations due to their collective redox properties.[108] OCPs are also easy to synthesize,[109,110] cheap,[41,111] environmentally stable[112] and biocompatible.[113] In below presented Table 2, some conjugated conducting polymers are enlisted with the range of their conductivities found to the highest values.[114]

Most common polymers are insulators and show high electrical resistance but properly prepared/treated OCPs can have advanced conducting or semiconducting properties.[115] This treatment known as doping, which significantly increases electrical conductivity of some OCPs. Electrical conductivity of OCPs makes them advantageous materials, which in addition have low-slung ionization potential, petite energy optical transitions and high electron affinity. Therefore, OCPs are suitable materials for the enhancement of sensitivity and better performance of various

**Table 1.** CNTs-based electrodes for the determination of heavy metal ions.

| Sr. no. | Electrode/modification procedure | Targeted metal Ion | Detection limit | Ref. |
|---|---|---|---|---|
| 1 | Cysteine modified CNTs | $Pb^{2+}$, $Cu^{2+}$ | 1 ppb, 15 ppb | [82] |
| 2 | Graphenated multi-walled carbon nanotubes (G-MWCNT) modified indium tin oxide electrode (ITO) | $Pb^{2+}$, $Cu^{2+}$ | 6 nM, 12 nM | [83] |
| 3 | Bismuth-modified carbon nanotube electrode (Bi-CNT electrode) | $Pb^{2+}$, $Cd^{2+}$, $Zn^{2+}$ | 1.3 $\mu$g/L, 0.7 $\mu$g/L and 12 $\mu$g/L | [84] |
| 4 | Paste electrodes of multi-walled carbon nanotubes | $Hg^{2+}$, $Cr^{2+}$ | 20 ng $\times$ dm$^{-3}$, 50–150 mcg $\times$ dm$^{-3}$ | [85] |
| 5 | Modified the carbon ink surface with different brands of multiwall carbon nanotubes (MWCNTs) and bismuth film (BiF) | $Pb^{2+}$, $Ca^{2+}$, $Zn^{2+}$ | 0.7 nmol/L, 1.5 nmol/L, 11.1 nmol/L | [86] |
| 6 | Sodium alginate decorated carbon nanotubes-graphene composite aerogel | $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$ | 1 $\times$ 10$^{-9}$ mol/L, 1 $\times$ 10$^{-7}$ mol/L, 2 $\times$ 10$^{-7}$ mol/L | [87] |
| 7 | Modified carbon paste electrode based on multi-walled carbon nanotubes (MWCNTs) and ligand (N-(4-hydroxyphenyl) ethanamide) | $Pb^{2+}$ | 7.5 $\times$ 10$^{-9}$ M | [88] |
| 8 | $C_{60}$ activated carbon and MWCNT modified glassy carbon electrode | $Hg^{2+}$ | 0.03 mM | [89] |
| 9 | Carbon nanotube-modified graphite electrodes | $Cd^{2+}$, $Pb^{2+}$, $Cu^{2+}$, $Hg^{2+}$ | 2.98 $\times$ 10$^{-7}$mol/L, 4.83 $\times$ 10$^{-7}$mol/L 3.81 $\times$ 10$^{-7}$mol/L 6.79 $\times$ 10$^{-7}$mol/L | [90] |
| 10 | Three-dimensional graphene–carbon nanotubes hybrid electrode | $Pb^{2+}$ $Cd^{2+}$ | 0.2 $\mu$g/L, 0.1 $\mu$g/L | [91] |
| 11 | Calixarene modified multi-walled carbon nanotubes | $Cd^{2+}$ | 10 mg/mL | [92] |
| 12 | Multi-walled carbon nanotubes modified by diphenylcarbazide | $Cd^{2+}$ | 0.05 ng/mL | [93] |
| 13 | Ag-CNT Electrode | $As^{3+}$ | 4.38 $\times$ 10$^{-5}$ mM | [94] |
| 14 | Multi-walled carbon nanotubes (MWNTs) as solid phase extractor | $Cu^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Co^{2+}$ | 30 $\mu$g/L, 0.45 $\mu$g/L, 0.60 $\mu$g/L, 0.35 $\mu$g/L, 0.57 $\mu$g/L 0.40 $\mu$g/L. | [95] |
| 15 | Iminodiacetic acid functionalized multi-walled carbon nanotubes | $Cr^{6+}$, $Pb^{2+}$, $Cd^{2+}$, $Co^{2+}$, $Cu^{2+}$, $As^{3+}$ | 1.2 ng/L, 0.70 ng/L, 0.40 ng L$^{-1}$, 2.5 ng L$^{-1}$, 3.4 ng L$^{-1}$, 0.79 ng L$^{-1}$ | [96] |
| 16 | Multi-walled carbon nanotubes (MWNTs) | $Cu^{2+}$ | 1.46 $\mu$g/L | [97] |
| 17 | Carbon Nanotubes (CNT) | $Cu^{2+}$ | 2.1 $\mu$g/L | [98] |
| 18 | Multi-walled carbon nanotubes (MWNTs) | $Mn^{2+}$, $Pb^{2+}$ | 3.5 $\mu$g/L, 8.0 $\mu$g/L | [99] |
| 19 | Modified carbon paste electrode based on multi-walled carbon nanotubes (MWCNTs) and nanosilica | $Pb^{2+}$ | 10$^{-7}$ mol L$^{-1}$ | [100] |
| 20 | Bimetallic Hg–Bi/single-walled carbon nanotubes composite electrode | $Zn^{2+}$, $Cd^{2+}$, $Pb^{2+}$ | 2 $\mu$g/L , 0.98 $\mu$g L$^{-1}$, 0.98 $\mu$g L$^{-1}$ | [101] |
| 21 | Screen printed carbon nanotube electrode (SPCNTE) | $Pb^{2+}$, $Cd^{2+}$, $Zn^{2+}$ | 0.2 $\mu$g/L, 0.8 $\mu$g/L, 11 $\mu$g/L | [102] |
| 22 | CNTs based nanoelectrode arrays (NEAs) | $Cd^{2+}$ | 0.04 $\mu$g/L | [103] |
| 23 | Carbon paste, modified with multi-walled carbon nanotubes | $Cu^{2+}$ | 1.1 $\times$ 10$^{-6}$ M | [104] |
| 24 | DNA functionalized carbon nanotube (DFC) | $Hg^{2+}$ | 0.05 nM | [79] |

sensors. Recently, environmental friendly conducting polymers modified carbon-based electrodes are replacing mercury electrodes.[116,117] Some OCPs in bioelectrochemical systems are functioning as redox mediators,[118] which promotes shuttling of electrons as well as protons between electrodes and electro-active reactants. In this way, OCPs-based electrodes can overcome the limitations of plain material (e.g. glassy carbon, graphite, gold, platinum, etc.) based electrodes.[119] In addition, some conducting polymers are biocompatible.[120,121,122] Therefore, they are suitable for the development of implantable sensors. Consequently, conducting polymer modified electrodes receive considerable attention in the detection of heavy metal ions because conducting

**Table 2.** Structures and conductivities of some of the most common conducting polymers.[54]

| Sr. no. | Polymers | Structure | Highest conductivity (S/cm) |
|---|---|---|---|
| 1 | Polyacetylene and analogs Polyacetylene | | 10$^3$–1.7 $\times$ 10$^5$ |
| 2 | Polypyrrole | | 10$^2$ –7.5 $\times$ 10$^3$ |
| 3 | Polythiophene | | 10–10$^3$ |
| 4 | Polyphenylene and analogues Poly(paraphenylene) | | 10$^2$–10$^3$ |
| 5 | Poly(p-phenylenevinylene) | | 3–5 $\times$ 10$^3$ |
| 6 | Polyaniline | | 30–200 |

**Table 3.** Electrodes based on OCPs applied for the determination of heavy metal ions.

| Sr. no. | Electrode/modified materials | Targeted metal ion | Detection limit | Ref. |
|---|---|---|---|---|
| 1 | Polyaniline-co poly(dithiodianiline) modified carbon paste electrode | $Pb^{2+}$, $Cd^{2+}$ | 0.03, 0.09 $\mu$g/L | [116] |
| 2 | A polystyrene-based membrane electrode | $Cd^{2+}$ | $3.16 \times 10^{-6}$ mol/L | [132] |
| 3 | Glassy carbon electrode modified by conductive polyaniline coating | $Pb^{2+}$, $Cd^{2+}$ | 0.1 $\mu$M, 0.13 $\mu$M | [133] |
| 4 | Polyaniline Sn(IV) tungstomolybdate Nanocomposite cation exchange material | $Pb^{2+}$ | $1 \times 10^{-6}$ M | [106] |
| 5 | Peptide-functionalized conducting polymer junction array | $Cu^{2+}$, $Ni^{2+}$ | 63 pM (4 ppt), 0.4 nM (23 ppt) | [134] |
| 6 | Langmuir–Blodgett films of functionalized polythiophenes | $Hg^{2+}$ | 0.1 to 100 ppm | [135] |
| 7 | Nafion-coated microelectrodes | $Pb^{2+}$, $Cd^{2+}$ | 0.3 ppb, 0.14 ppb | [136] |
| 8 | Poly(3-Methylthiophene) modified gold electrode | $Hg^{2+}$ | $3 \times 10^{-10}$ mol/L | [137] |
| 9 | Sonogel-carbon electrode modified with poly-3-methylthiophene | $Hg^{2+}$ | $1.4 \times 10^{-3}$/mol | [138] |
| 10 | PEDOT:PSS coated graphite carbon electrode | $Pb^{2+}$ | 0.19 nmol/L | [139] |
| 11 | Polyaniline Langmuir–Blodgett film modified glassy carbon electrode | $Ag^+$ | $4.0 \times 10^{-10}$ mol/L | [140] |
| 12 | Carbon paste electrode bulk-modified with the conducting polymer poly(1,8 diaminonaphthalene): application to lead determination | $Pb^{2+}$ | 30 ng/mL | [141] |
| 13 | N,N-dichromone-p-phenylenediamine modified carbon paste electrode | $Cu^{2+}$ | $10^{-5}$ mol/L | [142] |
| 14 | Polypyrrole film with electrochemically induced recognition sites | $Ag^+$ | $6 \times 10^{-9}$ M | [143] |
| 15 | Polypyrrole-modified electrode | $Pb^{2+}$ | $3.5 \times 10^{-9}$ M | [144] |
| 16 | Polythiophene-quinoline/glassy carbon-modified electrode | $Hg^{2+}$ | 0.4 ppb | [145] |
| 17 | Polyaniline and polyaniline–methylene blue coated screen-printed carbon electrode | $Hg^{2+}$ | $54.27 \pm 3.28$ $\mu$g/L | [146] |
| 18 | Polyacrylic acid/glassy carbon electrode (PAA/GCE) | $Pb^{2+}$, $Cd^{2+}$, $Co^{2+}$ | 0.9 nM, 1.9 nM, 11.0 $\mu$M | [147] |
| 19 | Poly (diphenylamine-co-2-aminobenzonitrile) (P(DPA-co-2ABN)) | $Cd^{2+}$, $Pb^{2+}$ | 0.255 ppm, 0.165 ppm | [148] |
| 20 | Surface ion imprinting strategy in electropolymerized microporous poly (2-mercaptobenzothiazole) films modified glassy carbon electrode | $Hg^{2+}$ | 0.1 nM | [149] |
| 21 | EDTA bonded 3′,4′-diamino-2,2′;5′,2′′-terthiophene on GCE | $Pb^{2+}$, $Cu^{2+}$, $Hg^{2+}$ | $6.0 \times 10^{-10}$, $2.0 \times 10^{-10}$, $5.0 \times 10^{-10}$ M | [54] |
| 22 | Polyviologen-modified glassy carbon electrode (PVGCE) | $Cu^{2+}$ | 0.02 ppm | [150] |
| 23 | Polymeric and chalcogenide glass membranes | $Cu^{2+}$, $Pb^{2+}$, $Cd^{2+}$, $Zn^{2+}$ | 0.2 nmol/L, 0.4 nmol/L' 0.06 nmol/L' 0.2 nmol $L^{-1}$ | [151] |
| 24 | Poly(4-vinylpyridine-co-aniline) (poly(4VP-co-Ani) | $Cd^{2+}$ | $7.94 \times 10^{-7}$ M | [152] |
| 25 | Glassy carbon electrodes (GCE) modified with poly (3,4-ethylenedioxythiophene) (PEDOT) | $Cd^{2+}$, $Pb^{2+}$ | 1.47 $\mu$g/mL and 1.15 $\mu$g/mL | [153] |
| 26 | Polyacrylic acid/glassy carbon electrode (PAA/GCE) | $Pb^{2+}$, $Cd^{2+}$, $Co^{2+}$ | 0.9 nM, 1.9 nM, 11.0 $\mu$M | [154] |
| 27 | PANI modified ITO electrode | $Cu^{2+}$ | 0.02 mM | [155] |

polymer modified electrodes enhance the stripping-based electrochemical responses.[123,124,125,126]

Many of the recent studies about OCPs come out with the conclusion that OCPs have functional groups capable for heavy metal ion binding. Sometimes these binding groups act as chelating sites for the binding of metal ions. Therefore, OCPs shows huge potential for metal ion detection and purification applications.[127,128,129,130] For example, conducting polymer poly(1,5-diaminonaphthalene) (PDAN) is one of such polymers, which is capable to chelate metal ions through its extra free amine group with the other amine group used for coupling with another monomer unit.[131] Table 3 represents the OCPs based heavy metal ion sensors.

## Composites based on organic conducting polymers/carbon nanotube for the detection of heavy metal ions

Recently, CNTs are almost becoming a benchmark for the performance of new nanomaterials in various applications.

However, CNTs have some limitations in their regular use. CNTs have bond structure based on sp2–sp3 hybridizations.[156] Thus, these properties have the close relation to the chirality, which are created by vacancies in CNTs structure. The existence of even small defects on CNTs surface, inner cavity, inner layers and outer part of CNTs, are responsible for the interaction of CNTs with metal ions.[157,158] The bundle structure of CNTs is responsible for the diminution of surface area. The low specific capacitance of pristine CNTs is also restricting their use in many applications.[159] Heavy metal binding capability of CNTs strongly depends on their iso-electric point, governed by adjusting the pH value of the solution. As pH is increased above the isoelectric point, unfortunately, the surface of CNTs getting negatively charged, resulting in CNTs are unable for electrostatic interaction with cationic species and leading to the desorption of metal ions. Thus, the detection of heavy metal ions through sorption method being totally dependent on the pH of the analyte, which is responsible for the contamination of CNTs surface.[158,160] The hydrophobic nature of CNTs and lack of functional binding groups on pristine CNTs

also leads toward weak adsorption of metal ions.[161] However, CNTs have some limitations toward ultra-trace detection of heavy metal ions due to the high background currents accompanying with their large surface area and absence of any functional group on the CNTs surface. CNTs modified with functional groups are a way to tackle these above-mentioned issues. Stability of CNTs in the harsh environment and surface fouling is still an unresolved issue.[73] Reproducibility and lifetime of the sensor are challenging issues, when these functionalized CNTs are tested in the harsh environments. Unfortunately, in all the above-mentioned techniques, CNTs hardly survive in the harsh environment in the sense that they get dislodged from the substrate in the detection process. Thus, there is great need to replace bare CNTs with new CNTs matrixes, which would eliminate above-mentioned issues.

Sensor electrode modified by MWCNTs functionalized by dithizone for the analysis of Cd(II) ions is reported.[162] However, large response time, short lifetime were the unresolved issues of reported sensor.

It has been verified experimentally and theoretically that OCPs are advantageous materials in the field of material science due to their high conductivity and high pseudo capacitance.[163] However, due to continuous charge, discharge process during repeated interpolation as well as depletion of ions, considerable volume change occurs in the OCPs, which is responsible for the reduction of mechanical stability.[164,165] One of the fundamental challenges in doped OCPs is the design of low band-gap organic conjugated polymers coatings.[166] The presence of an extended $\pi$-conjugation in OCPs polymers confers the required mobility to charges that are present on polymer backbone and makes them electrically conducting. However, the chains are rigid and possess strong inter-chain interactions resulting in the insoluble and infeasible material. Hence, lack of one of the easy processable properties of polymers. However, it can be controlled with lateral substitutes like CNTs can be made soluble without a significant decrease in their electrical conductivity after casting of the solvent.

Thus, many research communities have premeditated to utilize the ultimate properties of these two organic materials, OCPs and CNTs for the detection of heavy metal ions by overcoming their limitations and drawbacks. However, most of the advanced and outstanding properties of CNTs can extensively exploited by the incorporation of CNTs into polymeric matrix, and the formed composite materials can widen the gamut of more beneficial and attractive properties. The composition of conducting polymers with CNTs is applicable for a great variety of technological solutions. OCPs can provide more desirable properties compared to granular or ceramic composite materials together with amplified tensile strength, elastic modulus and better flexibility.[167] OCPs are widely used in the composite formation with CNTs due to their various advantageous properties like environmental stability, flexibility, lightweight, high conductivity, easy synthesis by chemical and electrochemical methods as well as a good processability. However, composite of CNTs with OCPs, can induce synergistic effects suitable for advanced applications.[168,169,170] CNTs/OCPs can act as efficient filler materials due to their high surface to volume ratio, when compared to that of other carbon

materials.[171] CNTs/OCPs composites formation follows the $\pi$–$\pi$ interactions between both components, which often lead to collaborative effects in improving electrochemical performances.[172] CNTs and OCPs are easy to bind and show strong interfacial coupling *via* donor–acceptor binding and $\pi$–$\pi$ interaction, $\pi$-electrons of CNTs can strongly interact with the quinoid ring of OCPs.[173,174]

One of the most widely studied and reported polymer, which is forming composite with CNTs and can, applied for the detection of metal ions, is nafion. Nafion increases the solubilization of CNTs.[175] Nafion increases the cation exchange capability and environmental stability. The most advantageous application of nafion/CNTs composite in the detection of metal ions is the replacement of mercury-based electrodes, which are environmental unfriendly and toxic.[73]

Nafion/CNTs composite in combination with bismuth has been applied for detection of trace Pb(II) and Cd(II) ions.[176] The composite structure improved the detection and reproducibility with good detection limits of 25 ng/L for Pb(II) and of 40 ng/L for Cd(II) ions. Sensor based on MWCNTs and nafion composite film modified glassy carbon electrode (GCE), which was suitable for the determination of Eu(III) ions with detection limit of 10 nM, has been reported.[177]

The sensor for detection of Pb(II) based on screen printed electrode modified by CNTs/nafion/(asparric acid) with sensitivity of 5.22 $\mu$A/$\mu$M has been reported in another research.[178] The performance of GCEs coated with polyaniline-multiwalled carbon nanotubes nanocomposite (MWCNTs/PANI) was investigated toward the determination of Pb(II) ions. It was observed that the MWCNTs/PANI coated electrodes had a better performance compared to that of the bare GCEs.[179]

The ultimate mechanism behind OCPs and CNTs composite is that, as prepared CNTs are conducting. However, CNTs primary disadvantage is that these CNTs are getting functionalized with limited functional groups, such as –COOH, –C = O and –OH. Moreover, CNTs are highly hydrophobic in nature. Therefore, unmodified CNTs have no specific affinity toward metal ions due to the absence of functional groups on their surfaces and cannot serve as good electrode material for metal ion sensing applications.[180] But OCPs have good environmental stability and chelating properties with intrinsic affinity toward heavy metal ions.[181,182,183] Thus, combination of OCPs and CNTs became a great combination, CNTs enables faster transfer of electrical signal due to its high conductivity and OCPs provides advanced affinity toward metal ions due to above-mentioned reasons. Consequently, CNTs and OCPs combination became suitable for the development of highly sensitive and selective metal ion sensors.

## Conclusions

This review is an effort to provide overview of CNTs- and OCPs-based electrochemical sensors for the detection of heavy metal ions. CNTs- and OCPs-based sensors are very promising due to their affinity toward analyte, lower detection limits, high sensitivity, selectivity, stability, etc. In spite of the successful use of these materials, there are still several limitations, which reduces practical and commercial application of CNTs- and

OCPs-based composites. It should be noted that, recently graphene and GO becomes very attractive for electroanalytical applications and electrochemical sensors, and new composites based on graphene and GO and conducting polymers will offer advanced performance of new electroanalytical systems. Hydrophobic nature, stability in harsh environments, surface contamination are the most threating issues for practical application of CNTs. OCPs also have some limitations such as the unpredictability of chemical structure and, low solubility, which reduces processing capabilities. Limitations of these materials can be successfully overcomed by the formation of their composites and utilization of individual ultimate properties of varios CNTs and OCPs.

## Acknowledgments

## Funding

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