Chapter

Application of Carbon Nanomaterials Decorated Electrochemical Sensor for Analysis of Environmental Pollutants

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Abstract

Carbon nanomaterials (CNMs), especially carbon nanotubes and graphene, have been attracting tremendous attention in environmental analysis for rapid and cost effective detection of various analytes by electrochemical sensing. CNMs can increase the electrode effective area, enhance the electron transfer rate between the electrode and analytes, and/or act as catalysts to increase the efficiency of electrochemical reaction, detection, adsorption and removal are of great significance. Various carbon nanomaterials including carbon nanotubes, graphene, mesoporous carbon, carbon dots exhibited high adsorption and detection capacity. Carbon and its derivatives possess excellent electro catalytic properties for the modified sensors, electrochemical methods usually based on anodic stripping voltammetry at some modified carbon electrodes. Metal electrode detection sensitivity is enhanced through surface modification of working electrode (GCE). Heavy metals have the defined redox potential. A remarkable deal of efficiency with the electrochemical sensors can be succeeded by layering the surface of the working electrode with film of active electro-catalytic species. Usually, electro catalysts used for fabrication of sensors are surfactants, nano-materials, polymers, carbon-based materials, organic ligands and biomaterials.

Keywords: nanomaterials, redox active site, carbon nanotube, surface functionalization, organic pollutants, electrochemical reaction

1. Introduction

Sustainable environment requires development of portable sensors for monitoring heavy and toxic metallic pollutants. Nanomaterials and nanostructures play a vital role as an adsorption sites into sensors [1] that leads to shift sensitivity, selectivity, multiplexed detecting ability towards high performance in terms of capability and portability [2]. Nanomaterials-based sensors exhibit an extremely high surface area, which can increase the number of binding sites [2] available for the adsorption of metal ions. Heavy metal pollution becomes a concern for global sustainability. Carbon nanomaterials [3] act as electrochemical sensors because they

have higher sensitivities, lower limit detection, and faster electron transfer kinetics than traditional detection electrodes [4]. An electrochemical sensor is an analytical device in which a recognition element is integrated within or intimately associated with a physical transducer [5] (an electrode) that transfers the analytical signal to an electronic circuit for the purpose of detecting a target analyte. The development of active electro catalysts plays a key role in the design of efficient, reliable, stable, and innovative sensing devices. Electrochemical detection is highly favored by the characteristics of rapid detection, high sensitivity and selectivity, high adsorption capability and large surface area [6]. Functionalized CNTs are good electrochemical sensing materials and can impart strong electro catalytic activity [7] to electrochemical reaction for most environmental pollutants such as heavy metal ions, organic pollutants containing electro active group. Environmental pollution is considered as a worldwide public problem, including heavy metals, inorganic/organic compounds, toxic gases, pesticides, antibiotics [8], bacteria, etc., which becomes a serious issues to human health and smooth environment [9]. The catechol (1, 2-dihydroxybenzene) is a phenolic compound which is extensively used in dye, petroleum refinery, plastic, antioxidant, cosmetics, medicines. The high toxicity and low degradability cause eczematous dermatitis, depression of the central nervous system (CNS) and a prolonged rise of blood pressure. With industrial development, many metal ions have discharged into natural environment. Unfortunately, metal ions, especial heavy metal ions, are easily caused soil and water polluted. Ordered mesoporous carbon have well-ordered and tunable porous structures and surface which have pore sizes in the range of 2–50 nm, Porosity offers high specific surface areas (more than 2000 m^2g^{-1}). However, the grafting of organic, inorganic or biomaterials into mesoporous carbon produces different functional groups and binding capacity which further improving their analytical performances. CNMs have received significant attention as candidate materials for detecting [10, 11] NO_x, NH_3, CO, SO_2 etc. For example, sensing of nitrogen oxide (NO_x), a major air pollutant emitted from power plants, which causes neurodegenerative diseases. The interfacial interaction can be enhanced by the surface-functionalization of nanotubes. The polar groups [12] on the nanotube surface increase the adsorption affinity of the electron-donor or acceptor pollutants and consequently offer better response. The detection of mercury ion at the Au-NPs interface is more sensitive and selective because they can form amalgam only with Hg compared to other metal ions. The electrochemical sensing performance had a relationship with the adsorption capacity, which excites the design of new sensing materials. The amino group on the surface of functionalized CMS [13] is bringing increased attractive force in adsorption of heavy metal ions. Though increasing the deposition time improves the sensitivity, it also lowers the detection limit because of the surface saturation at high metal ions concentrations. Carbon nanomaterials endowed with unique physiochemical properties were found to be most suitable for electrochemical detection of heavy metal due to their ease to modify, high sensitivity, good selectivity and high reproducibility. Unmodified CNTs are unable to chelate metal ions in aqueous solutions and cannot work as good electrode materials for the ASV analyses. The hydrophilic hybrid nanocomposites are able to adsorb heavy metal ions from aqueous solution due to the rich chelating groups. Carbon nano tubes (CNTs) exhibited effective adsorbent as well as sorbents for heavy metal ions. Therefore, it is reasonable to construct electrochemical sensors using the CNT or graphene-functionalized redox electrodes entity for detection of heavy metal because they are capable to detect simultaneously a majority of heavy metal ions with high resolution for defined and measured concentrations. The stripping techniques and particularly square wave and differential pulse anodic stripping voltammetry ensured alternative and extensive explored sensitive electrochemical

methods for heavy metal ions detection. The carbon bound Fluorine [14] exhibited both ionic as well as covalent interface and significantly enhanced the capacitive performance of fluorinated GO compared to pristine GO. Further, the fluorinated GO has high affinity for the simultaneous detection of heavy metal ions Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+} using square wave anodic stripping voltammetry (SWASV) as electrochemical tool. Fluorinated-graphene has gained great attention because of unique properties such as its high temperature resistance and enhanced electro catalytic activity. Electron withdrawing nature is arising from the strong electro-negativity of F and electron donating nature from the lone-pair electrons. Graphene or reduced graphene oxide (rGO) are used as an working electrode material; however, low sensitivity and potential interferences lowers their sensing capacity due to inherent irreversible agglomeration of graphene particle which excites researcher to develop green idea in the designing of native grapheme [15] based detecting electrodes as electrochemical sensor. Low sensitivity and poor selectivity related with the large over potential and the interference from the reduced sub-stance, such as oxygen, H_2O, encountered in the nitro aromatic compound (organic pollutants). Nitrophenols readily accumulate in organisms and are difficult to naturally degrade because of the high structural stability. The sensitivity can be improved by incorporating metal nano-particle over the surface of functional sites [16]. Owing to the high specific surface area, chemical stability, high p-conjugation and hydrophilic properties, GO can offer an excellent electrode platform for adsorbing other molecules. High surface to volume ratio with active sites, controlled distribution of pore size, exceptional sorption capacity and high sorption profi-ciency make CNTs suitable material for the development of electro-analytical systems dedicated for the detection of heavy metal ions. Hence, ionated CNTs play important role in the metal ion sensing due to their better ion exchange capacity. Oxidized CNTs have a great potential for cation uptake compared to non oxidized CNTs. In other words, non oxidized CNTs have tendency towards uptake of anions compared to oxidized CNTs. The presence of an extended π-conjugation in organic conducting polymer (OCPs) confers the required mobility to charges that are present on polymer backbone and makes them electrically conducting [17]. The sensing intensifier played a facilitating role between the GCE surface and the target metal ions by bringing analytes closer to transducer surface resulting in appearance of intense electrochemical signals. CNFs with high length-to-diameter ratio are capable of offering additional active sites for nanoparticle loading or deposition. The carbon nanotubes alone as well as in their oxidized and in their composite forms have tremendous ability to adsorb the heavy metal ions. Unmodified CNTs are unable to chelate metal ions in aqueous solutions and cannot work as good electrode materials. This is due to deficiency of functional group and sufficiency of hydrophobic environment. The effective combination of two carbon nanostructures can not only improve solubility and conductivity but also make up functional deficiencies [18]. Functionalization could significantly assist in the improvement of surface capacitance. Thus, the modified GCE exhibits good electro oxidative activity towards pollutants.

2. Nanomaterials extended electrochemical sensing platforms

Electrochemical Carbon Nanotube Filter Oxidative Performance [19] as a Function of Surface adsorption. The presences of surface resident reactive groups, or edge-plane like sites that are situated at the ends of their structures, and at defect sites, are responsible for the excellent electro catalytic activity of carbon nanoma-terials. Nanoparticles exhibited high surface to volume ratio with functional and

highly redox active core center leading to increasing the sensitivity and selectivity of the sensor. Thus, a highly active site has great affinity towards molecules result in molecule gets adsorbed on the surface of electrode to undergo a redox reaction. The conducting and chelating group has marked effect on the designation of sensor. Nanomaterials provide a special platform for the purification of contaminated water due to the high surface area of nano-sorbents and their capability of chemical modification and easier regeneration. NPs, QDs with some functionalization are used as tools, immobilization platforms [20] or electro active labels to improve the sensing performance exhibiting higher sensitivity and stability. The nano-particles and quantum dots [20] structures from the electrodes have significantly made a contribution to increasing the electro-catalytic properties because the functionalization of the structures could improve the high surface area, conductivity, stability, porosity, and mechanical rigidity.

2.1 Nanomaterials and its chemical functionalization

Nanomaterials have one dimension <100 nm [1] and possess physico-chemical properties dictated by their unusually small size, large surface area, shape and chemical composition. Nanomaterials usually require the surface functionalization for specific detection of metal ions. The p-type (anion doped) CNTs can behave as an electron deficient surface which can easily adsorb reductive molecule (NO_2) on its surface. The electrochemical sensitivity can be enhanced through attachment of active redox center either via physical or chemical forces over the reactive surface of carbon nanotube. Non-covalent functionalization normally involves physical forces (ion dipole, dipole–dipole, electrostatic force) for the binding of CNTs with catalysts (e.g., metal nanoparticles and metal oxides). Covalent functionalization [21] involves chemical forces (chemical reaction) for tagging of functional group with CNTs. In other words, it is realized through covalent attachment of chemical groups on the conjugated surfaces (edge, plane core) of CNTs. The number of oxygenated functional groups (e.g., –OH, –CO, and –COOH) created during calcinations, purification and isolation processes. As a result, controlled functionalities are susceptible to determine the sorption capacity of CNTs. These chemical groups greatly reduce the hydrophilicity and improve the capacity of ion exchanging behavior, leading to strong interactions with pollutants (e.g., heavy metal ions and organic compounds). Especially, the hydrophilic –OH and –COOH groups on the surface of CNTs exhibit superior sorption phenomenon towards low molecular weights and polarity. Their large surface area as pore volumes, functional surface groups and two basal planes are quite useful for the adsorption of pollutants. CNTs have been exploited in multiple electrochemical sensors because of their ability to facilitate electron transfer reactions [22] with electroactive species in solution and the electrode interface. *Thiruppathi et al.* reported functionalities of a carbon surface may assist the heavy metal ion adsorption properties. To improve their conductivity, FGO and GO were electrochemically reduced at −1.2 V for 300 s in a 0.1 M acetate buffer (pH = 5.0).Fe_3O_4 possessed electrostatic adsorption interaction with lead, and amine [13] acted as a better ligand displaying good chelation with lead. *Xiong et al.* designed amine –Fe_3O_4 modified glassy carbon electrode [23] as electrochemical sensor for detection of Pb(II) with a detection limit of 0.15 μM and 10.07 μA/μM sensitivity. Graphene-based nano-adsorbents are excellent advanced materials for the removal of the organic contaminants [24] from the water because of their nano-scaled size, high surface area, and ability to interact via pi-pi stacking. F-doped carbon nanomaterials have gained great attention because of unique properties such as its high temperature resistance, capacitance and enhanced electrocatalytic activity. The cross linked and bridged group exhibited high affinity and

attract environmental pollutants more efficiently. Strength of binding varies with functional group. The Hydrophilic HOOC-MWCNTs [25] can improve MWCNTs in synergistically electrocatalytic ability and adhesive ability. The introduction of organic, inorganic or biomaterials into ordered mesoporous carbon produces different functional groups which can tailor the sensing behavior.

3. Functionalized carbon nanomaterials and its sensing capacity

The functionalization of MWCNT [26] will give more active surface area and also the ionic interaction with anions would be more compared to the pristine MWCNT. The enhanced surface area and ionic interaction are very important for the real sample analysis at nanomolar concentrations, especially for the detection of harmful analytes. HOOC-MWCNTs [11] modified glassy carbon electrode (GCE) exhibited high sensing and adsorption capacity towards binary and ionic pollutants. The cyclic voltammetry resolve clear anodic peaks of SO_3^{2-} and NO_2^-. The anodic peak currents were gradually increases with concentration of ions. The peak separation between sulfite and nitrite are comparatively higher to probe the sensing of anions in nanomolar concentrations, it was found to be around 420 mV by cyclic voltammetry (CV) technique. This potential difference is highly attractive to determine the sulfite and nitrite simultaneously. The HOOC-MWCNTs decorated GCE had low limit of detection (LOD) of 215 nM and 565 nM for SO_3^{2-} and NO_2^-. The electrochemical sensing and detection was found to be two electron transfer oxidative reaction. The sulphate and nitrate ions were produced over the nano surface. *Sablok et al.* reported amine functionalized reduced grapheme oxide/carbon nanotube decorated novel electrochemical sensor for ultra-trace detection of Trinitrotoluene (TNT) up to 0.01 ppb with good reproducibility (n = 3). The sensing capacity was enhanced due to formation of charge transfer complex between electron rich surface of sensor and electron deficient ring of TNT. The binding of electron-deficient TNT to the amine [27] groups on the nano-sensor surface modulate electrical and optical properties of nano sensing elements. *Devi et al.* reported GCE/rGO-SH/Au-NPs [28] electrode as fascinating electrochemical sensor to analyze mercury ($Hg^{2+)}$ ions in the aqueous solution. The working electrode capture Hg^{2+} ions electrochemically and consequently get adsorbed on the redox active core surface followed by electrochemical oxidation by differential pulse voltammetry (DPV) with the increased oxidation current at +0.172 V. Moreover, this sensor platform revealed linear response for Hg(II) detection from 1–10 μM in phosphate buffer saline (PBS) solution and the detection limit was found to be 0.2 μM (S/N = 3). *Wang et al.* designed a GCE with MWCNT-CO-PANi [29] as a electrochemical sensor for detection of Pb^{2+} because the porous structure of conducting PANI surface can retard the bulk surface active compounds from reaching the sensing surface and thus minimizes the passivation of the working electrode. In addition, the PANI matrix offers binding capacity which can firmly hold the MWCNTs on the electrode surface. *Dai et al.* reported the improvement in stripping peak signals of heavy ions on PA/PPy/GO can be attributed to the high surface area of GO and the excellent electrical conductivity of PPy could enhance the electron transfer during the detection processes and peak intensity collaborated with number of functional groups with large negative charges on PA and GO is beneficial to improving the adsorption capacity of heavy metal ions. Phytic acid [30] consists of six membered rings with six phosphate group and two hydroxyl groups, could enhance complexation ability. **Figure 1(a)** shows strip peaks with resolved potential which demonstrates suitability of electrochemical sensor [30]. *Zhang et al.* reported size controlled AuNPs (5–15 nm)/CNFs/GCE electrochemical sensor for simultaneous tracing of

Cd(II), Pb(II) and Cu(II) with SWASV and detected three signal at −0.8, −0.5 and 0 V over a linear range of concentration 0.1 μM - 1 μM at a deposition potential of −1.8 V. *Mohamed Shaban* reported a porous Anodic Alumina (PAA) membrane was functionalized with $CoFe_2O_4$ nanoparticles and used as a substrate for the growing of very long helical-structured Carbon Nanotubes (CNTs) with a diameter less than 20 nm. The designed electrode was found to be suitable for detection of Hg^{2+}, Cd^{2+} and Pb^{2+} ions**. Figure 1(b)** indicates concentration dependent profile which demonstrates maximum range of concentration of detection for which sharp and intense peak appeared sensitively [30].

3.1 Design of selective electrochemical sensor

Ferrocene (Fc) functionalized MWCNTs works as a ratio metric electrochemical sensor. The Fc-MWCNTs/GCE modified sensor was used for detection of o-nitrophenol and p-nitrophenol present in water as toxic pollutants. When Fc-MWNTs/GCE [31] was dipped in 50 μM of o-NP and p-NP, the reduction peak of Fc remained fixed, but two well-separated peaks at about −0.66 V and-0.79 V could be detected which correspond to the reduced peaks of o-NP and p-NP, respectively. The process implies that the modified Fc can effectively separate the reduction peaks of o-NP and p-NP by about 0.13 V, which makes suitable it to detect o-NP and p-NP individually and simultaneously. **Figure 2(a)** demonstrates ferrocene functionalized MWCNTs as a ratio-metric and selective sensor [32]. **Figure 2(b)** indicates suitability of modified sensor and influence of metal nanoparticle on sensitivity [30].

3.2 Electro active carbon nanomaterials and its high surface density

Carbon nanomaterials mainly include zero-dimensional fullerene (C_{60}) and carbon dots (CDs), one-dimensional carbon nanotubes (CNTs) and carbon nanohorns (CNHs), Carbon nanofiber, two- dimensional graphene and its derivatives, and ordered mesoporous carbon (OMC). The hydrogen bonding interaction between the oxygenated groups of CNMs and hydroxyl groups has been utilized for the adsorption of pollutants containing functional groups (e.g., amine, hydroxyl and carboxyl groups. The CNF [33] is functionalized for improving its solubility and also remove the catalytic impurities for enhancing the electrochemical properties by

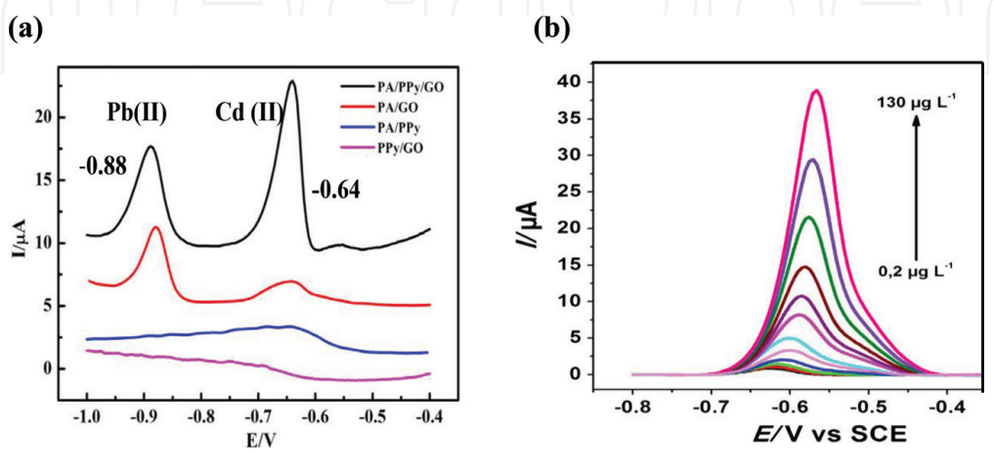

Figure 1.
(a) *DPV of PA/GO, PA/PPy, PPy/GO and PA/PPy/GO modified electrodes in 0.1 M acetate buffer solution (pH 4.5) containing 50 μg/L Cd(II) and Pb(II).* **(b)** *Calibration curve for Pb^{2+} determination, from down to up0.2, 0.5, 1, 5, 15, 20, 30, 40, 60,80, 100, and 130 μg/L Pb^{2+} in 0.1 M acetate buffer (pH 4.5) at PPy/CNFs/CPE under the optimized experimental.*

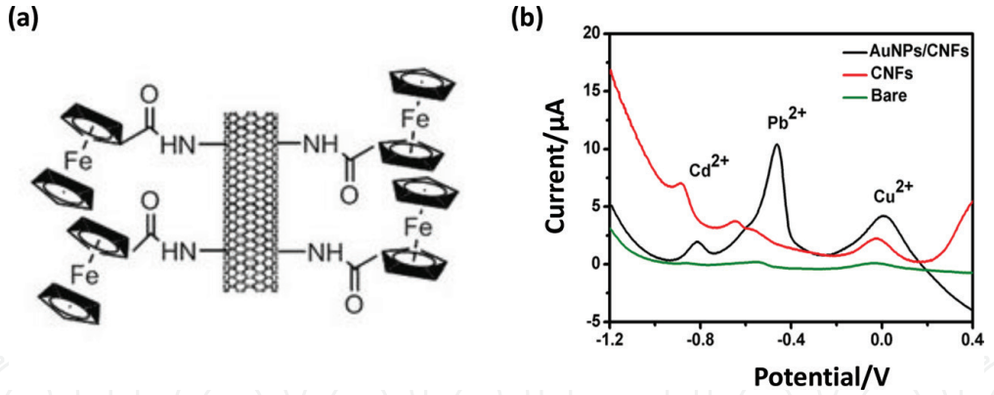

Figure 2.
(a) *Ferrocene functionalized MWCNT,* **(b)** *SWASVs for simultaneous detection of Cd^{2+}, Pb^{2+} and Cu^{2+} with the modified AuNPs/CNFs/GCE, CNFs/GCE and bare/GCE.*

the generation of more anchoring sites and surface reactive groups (carboxylic acid, hydroxyl, and carbonyl groups) on the open end and side walls of CNF. *Ramaraj et al.* reported $BiFeO_3$-F-CNF modified GCE is an effective electrode for electrochemical detection of catechol. The lowest value of ΔEp (0.106 V) and higher redox peak current response are indicating that $BiFeO_3$-CNF/GCE has faster electron transfer kinetics than that of other modified electrodes. The electrode is fabricated to anchor more recognition sites on the surface of the electrode and to achieve high affinity for the chemical adsorption of heavy metal ions. Polyaniline is combined with the rGO and glycine for strengthening the collective capacity for metal ions through nitrogen functionalities for example amine (-NH-) and imine (=N-) functional groups [13, 33]. Chitosan (CS) is a polysaccharide and its chemical modification can introduce new chelating groups along the CS chains, which can not only prevent its dissolution in acidic solutions but also improve the adsorption capacity and selectivity of an existing group for a specific metal ion. The MWCNT can be adhered through thiol functionalized Chitosan [21] which enhances the surface density to capture heavy metal ions. MWCNTs can lead to formation of good conduction pathway in the CS-SH film for better electro-analysis. *Li et al.* reported the simultaneous stripping analysis of Cd^{2+} and Pb^{2+} at the nitrogen doped carbon quantum dots modified grapheme oxide NCQDs-GO/GCE. The recorded ASV curves depict individual and highly resolved peaks at around −0.75 V for Cd^{2+} and − 0.50 V for Pb^{2+}, respectively. The peak to peak separation potential is about 0.250 V, which is large enough to recognize selective detection of Cd^{2+} and Pb^{2+} simultaneously. GO are served as a novel support to load nitrogen doped carbon quantum dots (NCQDs) and improve the conductivity and electron transfer rate of the hybrid. The AuNPs [34] modified working electrode can provide more electro active sites and faster electron transfer rate, all of which contribute to enhance the sensitivity of the simultaneous determination of Hydroquinone and catechol. It is difficult to simultaneously determine catechol and hydroquinone due to their overlapping peaks at ordinary electrode [35].

4. Analytical role of square wave anodic stripping voltammetry (SWASV)

Electrochemical techniques have the capability to maintain environmental interfacial processes at high rates and efficiencies by directionally and accurately controlling the electron transfer processes. An electrochemical technique where the analyte of interest is first electrodeposited onto the sensing electrode and removed

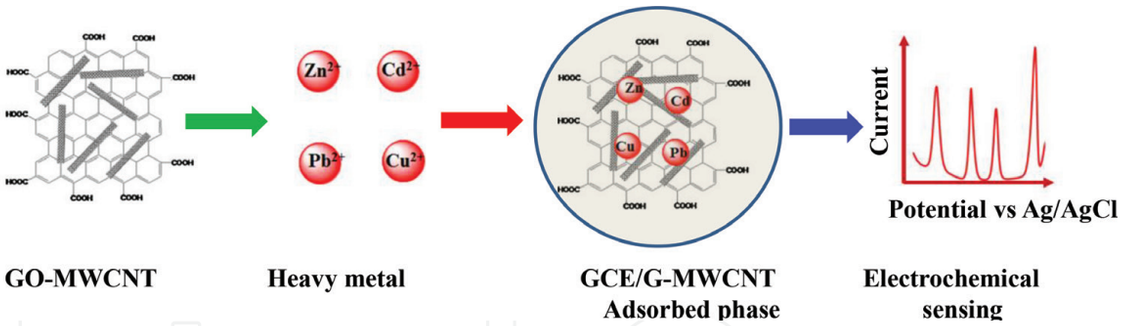

Figure 3.
General scheme of electrochemical sensing and detection of inorganic pollutants (heavy metal ions) through SWASV.

or 'stripped' with a sharp and intense peak by applying an oxidizing potential. During removal of pollutants, the peak current is measured as a function of time or function of the potential between the indicator (sensor) and reference electrodes. The redox probe is introduced as the inner reference to provide a built-in correction towards the signal transduction. The peak current ratio of analyte signal to probe signal is employed as the detected signal for analyte determination. The potential is varied as a square wave superimposed on a linear sweep. The potential separation between the stripping peaks can clear enough to distinguish the various heavy metal ions. The detection is expressed as sensing signals. The stripping peak currents are controlled by the amount of target metal ions adsorbed on the electrode surface. Striping peak current is directly proportionate to concentration of analyte. The SWASV is more prone over other voltammetry technique because of excellent sensitivity and unique ability to detect metals simultaneously. SWASV includes two independent procedures: deposition and stripping. First, in the deposition process (electrochemical reduction), metal ions can be reduced under a certain potential from the analyte solution to the working electrode. Inversely, when anodic potential is applied, the reduced metals are oxidized to their ions. Interference ions reduce the peak current for detected analyte during electrochemical analysis. Peak current varies with concentration of analyte and it increases linearly up to optimum concentration range which is also referred to as linear range concentration profile. Square-wave anodic stripping voltammetry is commonly used for metal detection due to its high sensitivity and low (nM–pM) detection limits. **Figure 3** indicates schematic sensing analysis and detected signal for pollutants [15].

5. Adsorption sites and its electrochemical sensitivity

The adsorption activity is related to the number of active functional groups on the surface of the carbon nanomaterials with highly oxidized surfaces showed a greater adsorption affinity for the stabilizers. Electro catalytic activity is related with hydrophobic or hydrophilic, positive or negative redox active groups of carbon nanomaterials. *Li et al.* reported MWCNTs are highly efficient to remove perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) from aqueous solution in light of their environmental persistence [36]. Bismuth modified CNT polystyrene Sulfonate (PSS) composite electrode for simultaneous detection of Pb(II) and Cd(II) by anodic stripping voltammetry. The designed composite electrode shows synergistic effect of bismuth and Polystyrene sulfonate. Since, polymeric dopant acts as cation-exchanger and CNT as an efficient signal transducer for sensitive and simultaneous detection of lead and cadmium. The detection limits were estimated to be 0.04 ppb for Pb(II) and 0.02 ppb for Cd(II) at 2 min accumulation. The presence

of MWCNTs can greatly enhance the conductivity of the hybrid nanocomposites and also make the GO plane unfold, whereas, the GO components can give the hybrid an important property to capture metal ions in aqueous. The CNT/rGO as nanohybrid materials exhibit strongly adsorption the organic components through the π-π interactions, a high electrical transport, and conductivities [37]. *Ruecha et al.* developed of an electrochemical sensor for simultaneous detection of Zn(II), Cd(II), and Pb(II) using a graphene–polyaniline (G/PANI) nanocomposite electrode in a linear working range of 1–300 μg/L. The anodic peak potential −1.31, −0.98 and − 0.75 V were recorded with well separation. **Table 1** shows different capacity for different electrochemical sensor towards inorganic /organic pollutants. The carbon nanomaterials are integral part of sensing materials. The CNMs are very prone to stabilize the structural integrity and reproducibility.

5.1 Influence of surface group (chromophores) and sensing sites

The electro catalytic properties of Carbon nanodots material depend on the presence of functional groups on the surface electrode because the material is a great electron acceptor and donor electron with the presence of some functional groups such as hydroxyl groups. Calixarenes [39] have three-dimensional spherical basket, cup or bucket shapes. **Figure 4(a)** depicts structural integrity of Calixarenes [39]. The spherical core volume is utilized in ion selective electrodes and membranes. It can capture stationary phases. The macrocyclic ring structure is efficient ionophores for metal ions viz. Na^{+}, Cd^{2+}, Pb^{2+} and Fe^{3+}. Coordination depends on macrocyclic ring size and ionic size of metal ion. Calixarenes can coordinate with the metal ions to increase the sensitivity of the electrochemical sensors. The metal ions, Fe(III), Cd(II), and Pb(II) gave a linear relationship with their concentrations at 1.0–10 nM on the CA/RGO/GCE.

Designed sensor/GCE	Pollutants	Sensitivity	LOD	Technique	Reference
GQDs-Au NPs	Hg(II)	2.47 μA/Nm	0.02 nM	SWASV	[38]
	Cu(II)	3.69 μA/nM	0.05 nM		
CA/RGO	Fe(III),Cd(II) Pb(II)	-	0.02 nM		[39]
Au NPs/CNF	Cd(II),Pb(II) Cu(II)	-	0.1 μM	SWASV	[32]
PAA-$CoFe_2O_4$/CNTs	Pb(II), Hg(II) Cd(II)	-	1 ppb	SWASV	[40]
CyS-MWCNT	Pb(II)	-	1 ppb	DPASV	[41]
	Cu(II)		15 ppb		
$BifeO_3$-CNF	Catechol	-	0.0015 μM	DPV	[42]
Gly/RGO/PANi	Cd(II)	15.20 μA/μM	0.07 nM	SWASV	[33]
	Pb(II)	41.3 μA/μM	0.02 nM		
CS-HS-MWCNTs	Hg(II)	36 μA/μM	3 nM	SWASV	[43]
CNPE-(CTS-ECH)	Cu(II)	212 μA/μM	10 nM	-	[44]
G/PANi	Zn(II)		1.0 μg/L		[45]
	Cd(II),Pb(II)	-	0.1 μg/L	SWASV	
PPy/CNFs	Pb(II)		0.05 μg/L	SWASV	[46]
NCQDs-GO	Cd(II)	-	7.45 μg/L	SWASV	[47]
	Pb(II)	-	1.17 μg/L	SWASV	
	Hydroquinone	-	0.17 μM	SWASV	[21]
AuNPs-HOOC-MWCNT	Catechol	45.53 μA/μM	0.89 μM	SWASV	
CNHs/GO	4-NCB	54.47 μA/μM	10 nM	SWASV	[48]

Table 1.
Different electrochemical sensor for detection of pollutants and analytical parameters.

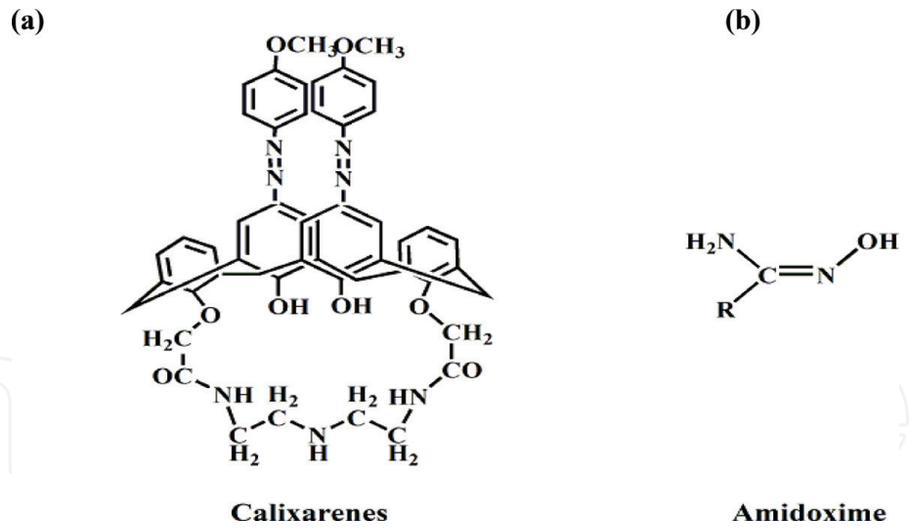

Figure 4.
Structure of organic compounds with core functional and sensing unit.

Different binding energies of functional groups have a great impact on absorption; weaker binding energies facilitate easier desorption [27]. As one of the best hydrophilic functional groups, the amidoxime groups modified on the electrode surface largely intensified the adsorption of heavy metals and lowered the impedance of the material when compared with an unmodified electrode. Amidoxime [49] group for functionalizing the carbon felt electrodes because of its superior adsorption ability for metal ions resulting from their coordination active sites. **Figure 4(b)** shows the structure of amidoxime [49]. The amidoxime group can coordinate with cations to form stable pentacyclic compounds, suggesting that this coordination bond should be stronger than other kinds of monodentate groups. The organic ligands having the amide functional moiety revealed strong and selective complexing ability towards metal ions when used to fabricate electrochemical sensor. The presence of carboxylate and pyridinium functional groups as negative and positive charge bearers over the surface of CNMs enhances the affinity of electrochemical sensing of cations and anions, respectively. The potential to modify carbon nanotubes with multiple chelating molecules with different selectivity towards various analytes attract designing of fancy sensor [12, 13].

5.2 Sensing reaction over electrochemical integrity

Composite phase provides more recognition sites on the surface of the electrode to achieve high affinity for the binding of inorganic pollutants. Conducting polymer enhances the collective capacity of carbon nanomaterials towards metal ions [33].

a. Accumulation/adsorption at working electrode

$$\text{Gly/RGO/PANi} + M^{2+}\ (\text{solution phase}) + 2e^{-} \rightarrow M^{0}\text{----Gly/RGO/PANi}$$

b. Anodic striping (electro analytical operation)

$$M^{0}\text{----Gly/RGO/PANi} \rightarrow \text{Gly/RGO/PANi} + M^{2+}\ (\text{solution phase}) + 2e^{-}$$

Highly efficient ionophores was developed for removing Cd^{2+} and Pb^{2+} using (PyTS-CNTs) [8]. The small conjugative surface is recalled 1, 3, 6, 8-pyrenetetrasulfonicacid sodium salt as the sensing material. The working window was from 1.0 μg/L

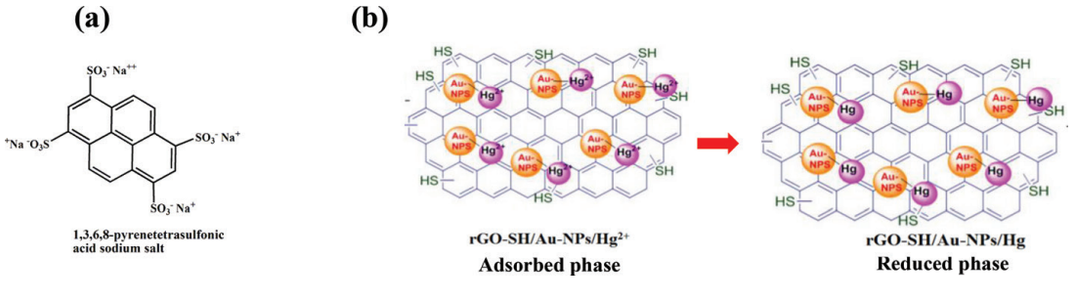

Figure 5.
(a) *Structure of functionalized pyrene.* **(b)** *Schematic representation for adsorption and electro-reduction of Hg(II) at rGO-SH/Au-NPs functionalized sensor.*

to 110 μg/L for both Pb^{2+} and Cd^{2+} ions. The limit of detection (LOD) was 0.02 and 0.08 μg/L, respectively. Functional groups greatly improve the hydrophobicity and ion exchange capacity, leading to strong interactions with pollutants. **Figure 5(a)** depicts the structural entity as a sulfonated salt of pyrene which can detect the pollutants through adsorption and ion exchange phenomenon [9]. **Figure 5(b)** demonstrates thiol and Au NPs anchor the adsorption and electrochemical reduction through enhanced charge transport [30].

5.3 Influence of cross linked structure and core integrity

Analytical performances of sensors are proportional to the surface concentration of the receptors. Cross-linking can enhance the electrochemical properties of electrochemical sensor. The CNT possess –COOH group. The cross linked and grafted CNT improve adsorption, adhesion, completion, chelation and ion exchange phenomenon along with fast charge transport [6]. This enhances selectivity and sensitivity. Cross linking increases the capturing integrity over the surface of carbon nanotube [43]. The chemical modifications of the chitosan by covalently attaching of selected molecules to the amino or hydroxyls groups can improve the ion-transport and ion-exchange proprieties of the biopolymer. Strong electron transmission from substituent (bridge) to carbon nanomaterial enhances the kinetics of sensing phenomenon [34]. *Janegitz et al.* developed functionalized carbon nanotubes paste electrode (CNPE) modified with cross-linked chitosan [crosslinked with glutaraldehyde (CTS-GA)] for determination of Cu(II) in industrial wastewater [44]. Chitosan is a cross linked [50] biopolymer having enriched $–NH_2$ and –OH functionality.

6. Factors influencing electrochemical detection

6.1 Nature and structure of sensor

The pore radius and pore volume decides enhanced redox peaks with much higher current and the kinetics of electro analytical process otherwise; signal distortion appears during detection of environmental pollutants. Different structures have different activation energy of adsorption and binding.

6.2 Deposition potential

The decrease in stripping current is attributed to the inadequate accumulation of the metal ions at lower negative potential and the initiation of hydrogen evolution reaction at a higher negative potential that may damage the surface of the electrode. The optimum deposition potential will resolve the ions efficiently and selectively.

6.3 Deposition time

The stripping peak currents show a linear increase with a prolonged period holding the maximum peak current which indicates the saturation of all the possible attachment sites on the functionalized electrode by the adsorption of the heavy metal contaminants.

6.4 pH (buffer capacity) of medium

The pH-value have significant influence onto the size of the square wave voltammetric peaks and also assists in the hydrolysis of metal ions, therefore, it is crucial to choose a suitable pH-value for the sensing of metal ions. At the high concentration of hydrogen ion, the intensity of peak current is reduced due to protonation of hydrophilic groups on the surface of sensing material which leads to the decrease in the attachment sites for the adsorption of the heavy metal ions. Proper pH maintains originality of electron rich functional group over the sensing integrity.

6.5 Supporting electrolyte

Supporting electrolytes are introduced to purge off the electro-migration effect. Therefore, the stripping voltammetric response of the peaks of current for the metal ions determination was also assessed by varying the nature of the stripping medium.

7. Conclusion and perspectives

In summary, non modified electrochemical sensor exhibited week binding and week adsorption capacity. The introduction and modification of surface functional groups was explored to improve the chemical selectivity and charge density at the active surface. The detection capacity can be improved through attachment of functional group having high affinity towards environmental pollutants. The electrochemical detection depends on the nature and structure of sensing electrode. The sensitivity and selectivity are critical core sites which enhances electrochemical analysis. CNTs enable faster transfer of electrical signal due to its high conductivity and conjugated polymers provide advanced affinity towards metal ions. Functionalized CNPs can result in highly sensitive redox sensors for a number of analytes. It can be demonstrated that the modified electrode showed excellent electro catalytic activity, increase the rate of electron transfer electron and the adsorption of the pollutants (inorganic/organic)molecules on the surface of the electrode.

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Conflict of interest

The authors have declared no conflict of financial interest.

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