Smart nano-architectures as potential sensing tools for detecting heavy metal ions in aqueous matrices

Tahir Rasheed[a]*, Sameera Shafi[b], Farooq Sher[c]

[a]*Interdisciplinary Research Center for Advanced Materials, King Fahd University of Petroleum and Minerals (KFUPM), Dhahran 31261, Saudi Arabia.*

[b]*Institute of Chemistry, The Islamia University of Bahawalpur, Bahawalnagar campus 62300, Pakistan*

[c]*Department of Engineering, School of Science and Technology, Nottingham Trent University, Nottingham NG11 8NS, UK*

*Corresponding author: Email address: tahir.rasheed@kfupm.edu.sa (T. Rasheed).

Abstract

The discharge of heavy metal ions into water resources as a result of human activities has become a global issue. Contamination with heavy metal ions poses a major threat to the environment and human health. Therefore, there is a dire need to probe the presence of heavy metal ions in a more selective, facile, quick, cost-effective and sensitive way. Conventional sensors are being utilized to sense heavy metal ions; however, various challenges and limitations like interference, overlapping of oxidation potential, selectivity and sensitivity are associated with them that limit their in-field applicability. Hence, nanomaterial based chemical sensors have emerged as an alternative substitute and are extensively employed for the detection of heavy metal ions as a potent analytical tool. The incorporation of nanomaterials in sensors increases their sensitivity, selectivity, portability, on-site detection capability and device performance. Nanomaterial based electrodes exhibit enhanced performance because surface of electrode at nano-scale level offers high catalytic potential, large active surface area and high conductivity. Therefore, this review addresses the recent progress on chemical sensors based on different nanomaterials such as carbon

nanotubes (CNTs), metal nanoparticles, graphene, carbon quantum dots and nanocomposites for sensing heavy metals ions using different sensing approaches. Furthermore, various types of optical sensors such as fluorescence, luminescence and colorimetry sensors have been presented in detail.

Keywords: Pollution; Smart nanomaterials; Heavy metal ions; Optical chemical sensors; Nanosensors and Aqueous matrices.

1. Introduction

Industrial, agriculture and domestic sectors are primary sources to discharge heavy metal ions in the eco-system. Some of the heavy metal ions like Zn^{2+}, Mn^{2+}, Fe^{2+} and Cu^{2+} are required by living organisms in trace amounts to carry the fundamental processes like metabolism, growth and development of different organs. While some of these heavy metal ions including Cd^{2+}, As^{3+}, Hg^{2+} and Pb^{2+} are considered toxic substances and contaminants even at very low concentrations that can be termed as a serious risk to the environment and human health [1-6]. Additionally, there are some natural sources such as erosion of soil and rock, rainwater and weathering from where heavy metals are also added to the environment [7]. On the other hand, leaching of metals from different sources like waste dumps, runoffs, livestock manures and roadwork are some of the other sources (secondary sources) of heavy metal pollution. Fig. 1 illustrates the primary and secondary sources of heavy metal pollution in the eco-system. Heavy metals occur in the form of ions, elements or complexes and are non-degradable.

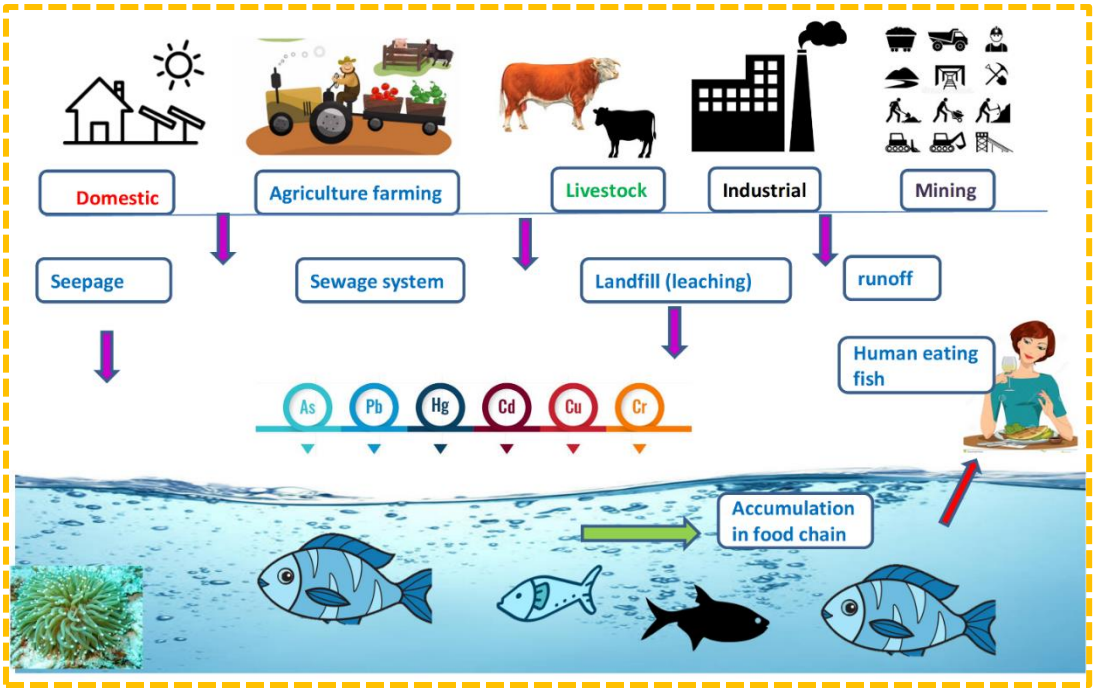

Fig. 1. Different sources of heavy metal pollution in the ecosystem.

Furthermore, heavy metals are elements with an atomic number of more than 20 and having a density of higher than 5 g/cm^3. They originally belong to metalloids, transition elements and post-transition elements [8, 9]. Their accumulation (even at a minute level) in the body causes severe health risks and most of them are carcinogenic [4, 10-17]. Maximum concentration limits and linked health risks related to heavy metals have already been reported in the literature [7]. The non-biodegradability, dissolution in water, ability to form aggregates in various parts of the body and delayed half-life makes these species more lethal to human life [18]. The mechanism of their toxicity involves their interaction with the cell proteins and DNA. This interaction leads to the change in protein conformation that in turn results in carcinogenesis. The other detrimental effects of heavy metal ions pollution on human life are lung damage, vomiting, nausea, high blood pressure, fatigue, hepatotoxicity, nephrotoxicity, neurotoxicity, headache and depression are the main causes of heavy metal ions toxicity (Fig. 2) [19].

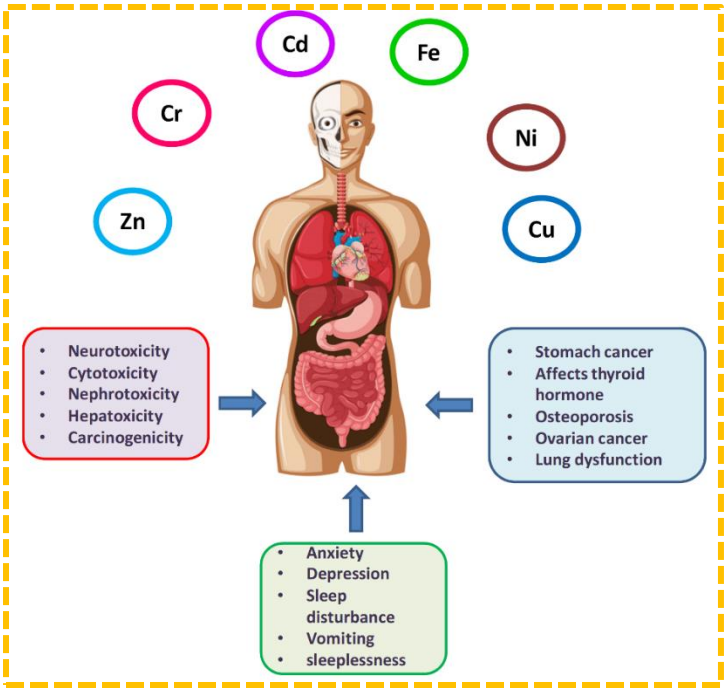

Fig. 2. Hazardous effects of heavy metals on human health.

Therefore, the accurate detection and determination of these toxicants is a pressing issue in recent years [20]. Some of the traditionally employed analytical techniques for the detection and determination of these metal ions include microprobes, X-ray fluorescence spectroscopy, capillary electrophoresis, ion chromatography, ultraviolet-visible spectroscopy, inductively coupled plasma-mass spectroscopy, atomic emission spectroscopy and atomic absorption spectroscopy [21-23]. These analytical techniques are selective and very sensitive however because of some limitations associated such as (1) High operating expenditures, (2) limits of hiring skilled individuals, (3) expensive and time intensive, (4) complex operating procedures (5) difficult sample preparation and (6) hard for real-time evaluation, limit their in-field applications [20]. This necessitates the development of a new technique that can detect these toxic metal ions with greater simplicity and accuracy. In this regard, chemical sensing has emerged as a promising modality for the accurate and on-site identification of these metal ions. Among a variety of chemical sensors, nanomaterial-based sensors are promising candidates for the purpose. The

emergence of nanomaterial-based sensors owes to their distinctive features such as great adsorption power, higher surface reactivity, higher catalytic efficiency and larger surface area [24-28].

A nanosensor consists of three components: (1) nanomaterial, (2) recognition element and (3) signal transducer. Several nanomaterials such as silicon materials, carbon-based materials and metallic nanoparticles (NPs) have been utilized widely to design a nanosensor. Fig. 3 portrays the design and working mechanism of various nanosensors. Nanosensors can be designed to sense a single analyte known as single plex or multiple analytes called multiplex. The higher degree of functionalization, the higher surface to volume ratio and higher reactivity enhance the nanosensor's sensitivity [29]. Furthermore, the formation of nanocomposites, organic-ligand attachment and covalent functionalization play a vital role to improve the selectivity and sensitivity in the identification of heavy metal ions. The reproducibility and lower limit of detection (LOD) are the other important parameters possessed by the nanomaterial-based sensors [22].

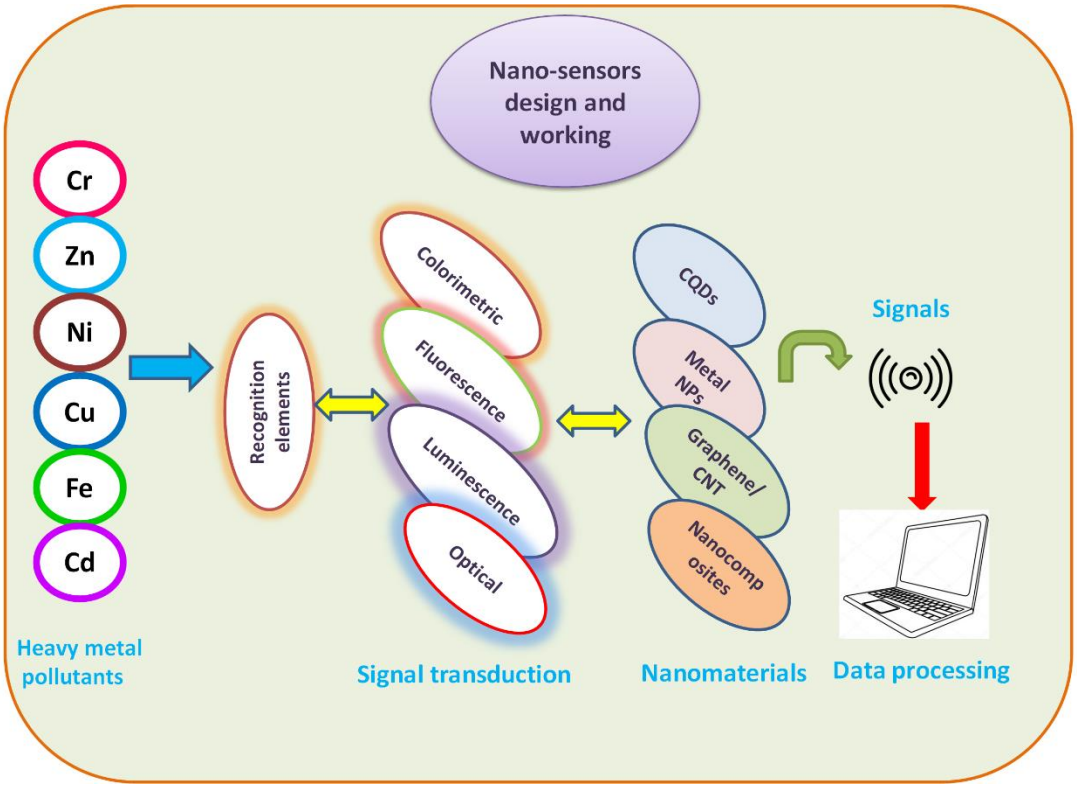

Fig. 3. Schematic illustration of design and working principle of various nanosensors for sensing metal ions.

This review emphasizes the modern advancement in the area of optical chemical sensors based on different nanomaterials. Furthermore, the designs, working and sensing mechanisms of nanosensors for the detection of heavy metal ions have been discussed in detail. Finally, the conclusion and future recommendations have been presented. Fig. 4 represents different types of nanosensors that are discussed in the present study.

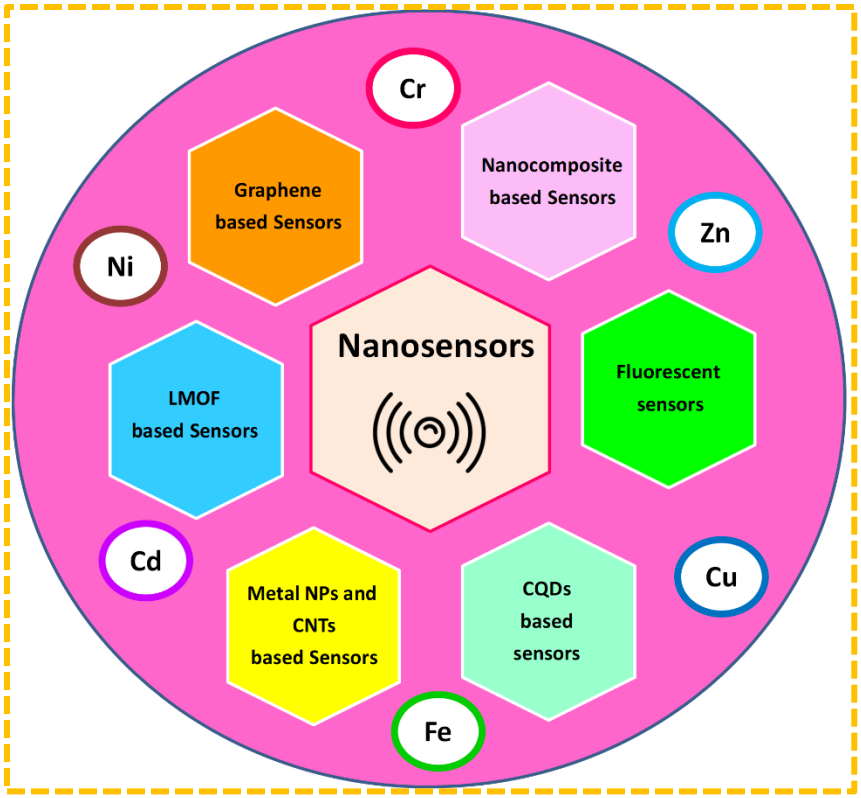

Fig. 4. Various types of nanomaterial-based nanosensors for the detection of heavy metal ions.

2. Optical sensors

Optical chemical sensors (OCSs) are widely employed for on-site identification of heavy metal ions. The transduction element of OCSs absorbs electromagnetic radiations for producing signals. The specific optical factors get changed by the interaction of radiation with the test sample that could be related to analyte quantity in the sample. Optical chemical sensors worked on the principle of variation of optical characteristics (lifetime, emission, transmission and absorption) because of the linkage of organic dye (immobilized indicator) with analyte [30, 31]. Target-induced-aggregation/anti-aggregation and surface alterations of nanomaterials may change the optical characteristics of nanomaterials chemical sensors based on the nanomaterial. In addition, the framework is dependent upon the suitable choice of solid matrix, with appropriate morphology,

functionalization and immobilization strategies for these constituents [32]. Fluorescent, surface plasmon resonance (SPR) sensors, surface enhanced Raman scattering (SERS) optical sensors, fluorescence and luminescence sensors have also been demonstrated in this review. Special focus is given to utilization of nanomaterials in the development of these sensors.

2.1. Fluorescent sensors

Fluorescence based nanosensors consist of the fluorescent element that signals receptor component and binding site to bind the particular analyte [11-14, 33-35]. Quantum dots (QDs) have been extensively employed as an alternative to the dyes-based fluorophore. The unique optical characteristics such as high stability towards photo bleaching, narrow emission, great quantum yield and wide range of absorption spectra as well as excellent H_2O solubility, great photo-stability and changeable quantum size in a broad emission range make QDs promising alternatives for sensing and biosensing of a variety of analytes [36, 37]. Because of broad excitation profiles, multiplexed detection potential, higher quantum efficiencies, size dependent fluorescence emission peaks, great photostability and narrow emission spectra the quantum dots are advantageous to employ as fluorophores [38]. The structures of graphene QDs (GQDs) and carbon dots (CDs) are free from heavy metals.

Moreover, these contain extraordinary surface functionality and very good biocompatibility that makes them very effective candidates for the fluorescent identification of metals [39, 40]. Selective linkage sites are formed on the sensor surface that is permitted by molecular imprinting that assists particular linkage of analytes. The facile synthesis and stability are major advantages of formed sensing materials. Based upon the ion-imprinted dual emission quantum dots nanohybrids ($CdTe@SiO_2@CdSe$) the ratiometric-fluorescent probe has been developed for the identification of Cd^{2+} ions in aqueous samples [41]. Probe structure was found based on covalently bonding

green emitting CdSe QDs at the surface of silica nanoparticles that was surrounded by red emitting CdTe QDs. By chemical etching with ethylene-diamine tetra-acetic acid, the particular Cd^{2+} ions detection sites upon the surface were formed that extinguished the fluorescence (green) of CdSe quantum dots on nanosensor's external side. By exposing nanohybrid to various quantities of Cd^{2+} ions, the green fluorescence is progressively reinstated and internal red fluorescence remains the same. As a result, the identifiable fluorescence of different colors was perceived when it is in contact with Cd^{2+} ions. The ratiometric sensor showed very good sensitivity at optimized conditions with LOD of 25 nM. Another study, reports the development of unique luminescence solid state material (QD-LDH) for on-site concurrent identification of Hg^{2+}, Cd^{3+} and Pb^{2+} ions in H_2O [42]. The architecture of the nanosensor is based on layered double hydroxides (LDH) and manganese-doped ZnS QDs capped with the glutathione (GSH-Mn-ZnS QDs). The LDH function inhibits the accumulation of quantum dots (QDs) in solid nanocomposite and improved luminescence in aqueous solution as compared to the dispersed quantum dots. Moreover, the chemical and thermal stability of quantum dots is also strengthened by LDH containing nanocomposite. A turn-off response was observed by the introduction of Hg^{2+}, Cd^{3+} and Pb^{2+} ions. The luminescence intensity of nanosensor disappeared as the nanosensors come in contact with analytes. Remarkable sensitivity and selectivity were portrayed by the sensor with LOD of 0.93 μM for mixed metal ions. Likewise, the identification of Hg^{2+} ions in raw-water and tape water samples was carried out with the help of nitrogen-doped-carbon based nanosensor QDs (N-CQDs) that was hydrothermally synthesized as a fluorescent probe [43]. The formation of sensor utilized folic acid (carbon and nitrogen source). For label-free identification of Hg^{2+} ions the prepared N-CQDs (size approximately 4.5 nm) assisted as a sensitive sensor. Noteworthy quenching of fluorescence intensity is driven by the introduction of Hg^{2+} ions that lead to non-radiative electron

shift from the high energy states to Hg^{2+} ions d-orbital. The N-CQDs have shown specificity for Hg^{2+} ions within the existence of a great quantity of other various competitive metal ions and can be termed as "turn-off" fluorescent sensors. The LOD was calculated as low as 0.23 mM. In another documented report, the Gold nano-clusters based CdTe quantum dots were developed. The prepared nanocomposite material showed high selectivity and sensitivity towards fluoride and Hg^{2+} ions. This nanosensor was developed from a bovine-serum-albumin protein-conjugated Au nanocluster and from tripeptide-capped CdTe quantum dots [44]. The salt-initiated conglomeration upon introduction of Hg^{2+} ions driven to critical reduction approximately up to 74% of nanosensor photoluminescence. The LOD towards Hg^{2+} and fluoride ions was determined as 9 and 117 nM respectively.

Graphene oxide (GO) is another useful nanomaterial that is non-toxic and contains a carboxylic acid group that could be utilized to conjugate the various biomolecules and deoxy-ribonucleic acid functionalized with amine by a covalent bond. Further, GO is an economical fluorescence radiation quencher (acceptor) that may be easily formed on large scale. The fluorescent features of GO can easily be tuned by modifying the surface functionalities. Therefore, graphene oxide obtained great consideration in sensing heavy metals [45]. Ju and his colleagues [39] revealed a simple technique to synthesize the greatly fluorescent nitrogen-doped GQDs (N-GQDs) for the identification of Fe^{3+} ions. GQDs are treated hydrothermally with hydrazine for the preparation of N-GQDs as a sensing platform. The presence of oxygen based functional motifs in N-GQDs showed improved fluorescence potential with the blue-shifted-energy that may be due to the existence of nitrogen (electron withdrawing nature) in the structure of nanosensor. The PL intensity of N-GQDs has been reduced by the incorporation of Fe^{3+} ions. This reduction in PL owes to the chelation of Fe^{3+} ions with nitrogen (N) of N-GQDs. In real water samples, the LOD of 90 nM was determined by

the job's plot method. Through the electrolysis of graphite, the sulfur-doped-GQDs (S-GQDs) synthesis has been reported [40]. The S-GQDs showed a more sensitive response to Fe^{3+} ions in comparison to B-GQDs, GQDs and NGQDs. Noteworthy, reduced fluorescence intensity for SGQDs was noticed at 0.7 mM for Fe^{3+} ions concentration on the other hand the fluorescence of B-GQDs, GQDs and NGQDs remains unaltered. Greater sensitivity in human serum (with LOD of 4.2 nM) was displayed by a probe. For the identification and recognition of Fe^{3+} ions atoms in H_2O, the greatly selective and sensitive graphitic CQDs (GCQDs) were developed through electrochemical ablation of graphite electrodes [46]. The solubility of the probe in water was improved by oxygen containing functional moieties (-COOH and -OH). Moreover, because of the development of complexes between phenolic -OH moieties of GCQDs and Fe^{3+} ions the probe showed greater sensitivity (LOD of 2 nM). By exfoliation of graphene oxide into the graphene oxide (GO) sheets through ultra-sonication in aqueous media, the GQDs based developing zero-D-materials synthesized within a range of 3 to 20 nm. In conjunction with the best surface grafting feature, the material also contained carrier transport portability, great surface range and predominant chemical and thermal steadiness. Ran and his co-workers [47] utilized GQDs and silver-based nanoparticles embodied GQDs (AgNPs/ GQDs) for recognition of Ag^+ ions and bio-thiol molecules as glutathione (GSH), cysteine (Cys) and homocysteine (Hcy). The FL intensity of novel fluorescent material GQDs was decreased after incorporation of Ag^+ ions. The reduced fluorescence that was dosage-dependent owes to the synthesis of AgNPs/GQDs hybrids. In addition, when bio-thiols were introduced into the solution, the fluorescence of GQDs was diminished and it has been accredited to Ag-S bond formation. The probe demonstrated ultra-sensitivity with LOD of 3.5 and 6.2 nM for Ag^+ ions and Cys respectively. Lu and coworkers [48] exhibited single-step sulfur and oxygen co-doped graphitic carbon nitride QDs (OS-GCNQDs)

synthesis through a reaction between thiourea and citric acid in warming conditions. The synthesized OS-GCNQDs showed great quantum yield (14.5%) and demonstrated variable fluorescence responses in the existence of various metal ions in similar conditions. The PL intensity of OS-GCNQDs has been quenched through the incorporation of the Hg^{2+} ions that could be because of great affinity of thiourea moieties and amino functional moieties existing on the surface of nanocomposite with Hg^{2+} ions. The OS-GCNQDs ascertained greatly sensitive that was capable of selectively towards Hg^{2+} ions with LOD of 0.37 nM. Similarly, other documented reports also investigated the detection of heavy metal ions in aqueous media through graphene and graphene oxide-based optical sensors [48, 49]. The addition of graphene oxide or graphene in the nanosensors potentially enhanced the sensitivity in heavy metal detection. For sensing heavy metal ions, metal-based nanomaterials have been widely employed because of their great biocompatibility, easy fabrication, plasmonic features and optical characteristics [28, 50, 51].

To enhance the detection of heavy metals, metallic nano-structures consisting of aluminum, silver and gold plasmonic NPs have been broadly utilized [52]. For spectral sensing of heavy metals, one-step preparation of CuS, NiS & ZnSNPs, CuSNPs and NiS NPs has been reported [53]. By utilizing tri-sodium citrate and sodium sulfide, the prepared nanoparticles were stabilized in aqueous media. For spectral detection of Pb^{2+}, Cd^{2+} and Hg^{2+} ions at very low concentrations, the solid nanoparticles were being utilized as optical sensors. In the existence of ions of heavy metal, absorption potentials of nanoparticles have enhanced and this was connected to basic accumulation of NPs or variations within the nearby atmosphere of the nano substances that produced variations within characteristic surface-plasmon-resonance. For Hg^{2+} ions identification, NiS NPs were found beneficial while CuS NPs and ZnS NPs were found capable to identify Hg^{2+}, Cd^{2+} and Pb^{2+} ions with LOD of 0.1-1 mM and 0.1-1.5 mM, respectively. Li and his colleagues [54] demonstrated the

fluorescent nanoprobe based upon L-cysteine (L-Cys) capped Fe_3O_4@ZnO (Fe_3O_4@ZnO@ L-Cys) for profoundly specific Fe^{3+} ions identification. Upon the addition of Fe^{3+} ions solution, nanosensor fluorescent potential was quenched. This was connected to the interaction of Fe^{3+} ions with L-Cys. With LOD of 3 nM/L, over a series of competing ions such as Co^{2+}, Mn^{2+}, Cu^{2+}, Cd^{2+}, Mg^{2+}, Al^{3+} and Pb^{2+} ions the nanoprobe showed high selectivity in identifying Fe^{3+} ions in serum and wastewater (Fig. 5).

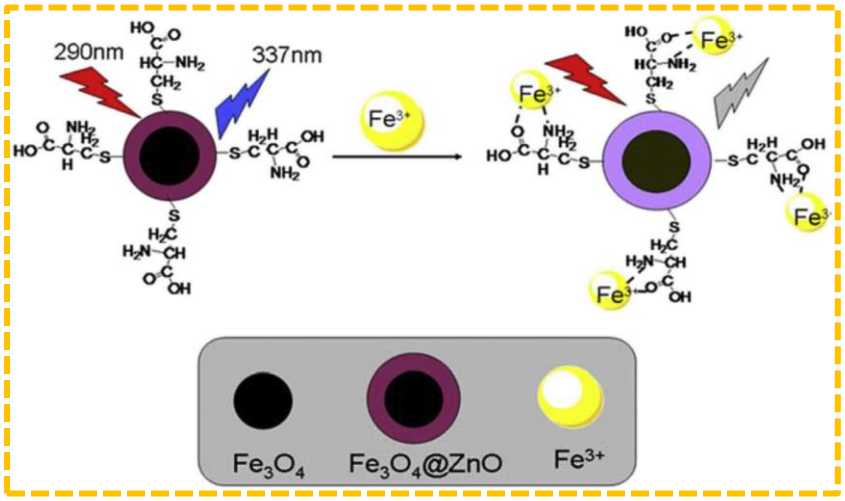

Fig. 5. The binding mechanism of Fe_3O_4@ZnO@L-Cys with Fe^{3+} [54]. Licensed under a Creative Commons Attribution 4.0 International License.

Shahat and his coworkers [55] synthesized MSNPs based functional material, wherein organic ligand, N,N' di (3- carboxysalicylidene)-3,4-diamino-5-hydroxypyrazole (DSDH) was attached to the mesoporous silica (MS). Through Vander-Waals forces, covalent bonds and hydrogen bonding the plenteous hydroxyl moieties on MS surface allowed conjugation of DSDH. The obtained material was employed for Co^{2+} ions identification in aqueous media. The absorbance intensity of the probe was enhanced by introduction of Co^{2+}. This was credited to the interaction between Co^{2+} ions with DSDH. With LOD of 0.24 mg/L, the probe demonstrated to be sensitive in recognizing Co^{2+} ions. The synthesis of conjugate nanomaterials (CNMs) has been accomplished with the

ligand (organic), ammonium (4-chloro-2- mercaptophenyl) carbamodithioate (ACMPC) that consist of sulfur donor element by utilizing a coordinate reaction approach by functionalizing MSNPs. In another study, Awual and coworkers [56] documented a ligand conjugated nanomaterial for Hg^{2+} ions identification in an aqueous solution, the resultant sensor was found selective and sensitive toward analyte. As within the case of DSDH, through reversible covalent bonds, Vander Waals force and hydrogen bonding the attachment between SNPs and ACMPC occurs. The color variation from colorless to yellow led to enhance in intensity of absorbance on the addition of Hg^{2+} ions to CNM solution at optimum pH 5.2 and this was observed through ultraviolet-visible spectroscopy. The formation of (ACMPC)-Hg^{2+} complex was credited to the selectivity of CNMs. With LOD of 0.26 mg/L, the nanosensor showed high sensitivity in identifying Hg^{2+} ions. Cao and his coworkers [57] have prepared mono-layer graphite type C_3N_4 (g-C_3N_4) as a fluorescence sensor for Ag^{+} ions identification in real H_2O. The sensor reached a LOD of 52.3 nmol/L in optimized conditions for the Ag^{+} ions without obstructions to the co-existing of miscellaneous metal ions such as Cd^{2+}, Al^{3+}, Ca^{2+}, Ni^{2+}, Co^{2+}, Mg^{2+}, Pb^{2+}, Mn^{2+}, Zn^{2+}, Hg^{2+}, K^{+}, Be^{2+}, Fe^{3+} and Ba^{2+}. Additionally, the obstructions of co-existing Cu^{2+} ions within the sample could be screened by EDTA chelate incorporation. Preparation of nano-aggregates of pyrene polymer as a probe (fluorescent) for identification of Sr^{2+} ions in solution has been reported [58]. With LOD of 9 nM, the fluorescent intensity of the probe quenched upon the addition of Sr^{2+} ions. Over a broad range of competing metals ions such as Pb^{2+}, Hg^{2+}, Cd^{2+}, Zn^{2+}, Ag^{+}, Co^{3+}, Cu^{2+}, Mn^{2+}, Fe^{3+}, Al^{3+}, Ba^{2+}, Mg^{2+}, Ca^{2+}, Cs^{+}, K^{+}, Li^{+} and Na^{+}, the nanosensor displayed high selectivity for detection of Sr^{2+} ions. The hydrophobic nature of pyrene moieties permitted them at first step stacked in water that driven to excimer emission. Attachment of the Sr^{2+} ions to host gave

alterations in conformation that formed the cavity to fit Sr^{2+} ions by enhancing gap between pyrene (two) motifs. Consequently, the nanosensor fluorescence intensity was quenched.

3. LMOFs implication for detecting Persistent metal ions

Herein, metal ions can be classified into three major categories. The group that is detected in a broader sense using LMOFs essentially Al^{3+}, Hg^{2+}, Fe^{3+}, Cu^{2+}, Cr^{3+} ions, the other group of metal ions comprise Eu^{3+}, Tb^{3+}, Sm^{3+}, Dy^{3+} ions called repetitive metal ions and lanthanide Ln^{3+} metal ions respectively, whereas the third group of metal ions is hardly detected using LMOFs. Moreover, the detection limit, applicable strategies, sensitivity, selectivity, structure signal, mechanism response relationships and parameters like Stern -Volmer constant for each metal ion can conduct an efficient sensing approach with adequate detection considerations.

3.1. Detection of mercury (II)

Facile and faster detection of Hg^{2+} ions for human safety from a catastrophe such as Minamata, whereas LOD is 2 µg/L reported by US Environmental Protection Agency. There are varied methodologies implemented for Hg^{2+} ions sensing utilizing LMOFs, for example, 1D constituting MOF-composites [59], ratiometrically 2-dimensional detectors [60], chemo-dosimeter detector comprised of MOF [61], approach for probing 2D-dual solvents [62], (d)-LMOFs [63], 2-dimensional probes [64], lanthanide(+3) ions applied for post-improvement of (d)-LMOFs [65], implications of coordination-polymer-nanoparticles (CPNPs) [66]. There are many fruitful merits and incompetent demerits that have been noticed in every category. After the post-synthetic incorporation of Eu^{3+} ions, Eu^{3+}/CDs@MOF-253 composite represents simultaneously both the CDs centered emission (ICD) and characteristic sharp emissions of Eu^{3+} ions originating from the Eu^{3+} ions lowest emitting state. Further, IEu^{3+} showed no considerable variation while 1-dimensional quenching effect was revealed in IQDs by way of enclosed quantum dots (QDs)

surface-association of oxygen atoms and Hg^{2+} ions. Consequently, an increment of 7.5 multiple was indicated by IEu^{3+}/IQDs, in comparison to the primary ratio. Proficient discriminativeness of Eu^{3+}/QDs@MOF-253 having 13 nM LOD for Hg^{2+} ions affirmed such effect merely in Hg^{2+} ions, although different metal ions were also available. In addition, Hg^{2+} ions could cause red coloration altered from blue suggesting the above-mentioned composite to perform like colorimetric probe [60]. Remarkable chemical alteration including covalent bond manufacturing and splitting provides the basis for non-reversible conversion of obvious signal accompanying identification of analyte using chemodosimeter sensors.

Owing to the existence of bulky butyne groups, rotation of carbonyl group was hindered resulting in FL responsive UiO-66@Butyne. Through an irreversible oxymercuration reaction, UiO-66@Butyne exhibits a 1D quenching response to Hg^{2+} ions. The loss of alkyne functionality was shown by a decreased peak at 2950 cm^{-1} in FT-IR spectroscopy after treatment with Hg^{2+} ions. The presence of concentrated sulfide is unfavorable because compounds comprising sulfur and nitrogen atoms experience oxidative cleavages at ambient conditions when preserved for a longer duration, although Hg^{2+} ions have been appropriately diagnosed via LMOFs inhabiting these moieties. These display non-renewable sensitivity in comparison to other probes like fluoro-/chemo-sensors. Fabrication of linking agent-functionalized (d)-LMOFs has been considered a high potential category for sensing Hg^{2+} ions. Nitrogen donor-guest communication parts are a vital constituent of functional ligands [67], sulfur-supported were on the other hand [63] also few residing oxygen units [67]. Scarcely, variation in molecular design or molecular breakage could affect the procedure of identifying Hg^{2+} ions [63]. Detection-limit of 9.9 pM demonstrated higher sensitivity for Hg^{2+} ions by a zinc-based MOF with the representation of [{Zn(4,4′-AP)(5-AIA) }.(DMF)]$_{0.5n}$, and proved with photoluminescent measurements. The introduction of Hg^{2+} ions

brought a change in the stretching peak position of carbon and nitrogen bond as shown in FT-IR measurements. Moreover, nitrogen (1s) X-ray photoelectron spectroscopy measurements for [{Zn(4,4′-AP)(5-AIA) }.(DMF)]$_{0.5n}$ shows a peak at ~403.57 eV for coordinated-amino group, ~402.36 eV for azo-group and ~399.10 eV for pyridine-group, enclosed in a wide peak at ~400 eV. Interaction of Hg^{2+} ions with [{Zn(4,4′-AP)(5-AIA) }.(DMF)]$_{0.5n}$ residing nitrogen units resulted in shifting of peaks in the redder zone around ~405.53 eV, attributable to Hg^{2+} ions incorporation. The Hg^{2+} ions receive electrons from azo-groups during communication of N_2 group with Hg^{2+} ions as displayed by the practical investigations. Until now, literature explained higher K_{SV} and LOD for responsive and discriminative identification of Hg^{2+} ions adopting particular soft N-constituting impressive architecture of d-LMOFs. Formerly, a small FL shoulder is exhibited at around 410 nm while a bright Photo-luminescent radiance has been noticed at around 350 nm for Cd-EDDA skeleton. The above given explanation corresponds to LLCT and LMCT reactions (processes), accordingly [64]. The use of Cd-EDDA in metal ions sensing reveals that as the Hg^{2+} ions concentration rises that is connected to the LMCT process. The obtained Stern-Volmer constant (KSV) 4.3 mM and identification-limit 10 nM were observed in the presence of 0.21 mM Hg^{2+} ions and 8.2 times improvement with the given ratio. Ligand's reformation and the existence of Hg^{2+} ions were considered the fundamental requirements for Cd-EDDA compound breakage which consequently reduced LMCT and were confirmed with mass-spectroscopy, FT-IR and PXRD. Thus, in the event of rapid simultaneous presence of LLCT and LMCT processes in PL emission of (d)-LMOF, the ratio of ILLCT/ILMCT may be considered as a 2D ratiometric response in the sense that when the framework collapses, the ratio of ILLCT/ILMCT may be considered as a 2D ratiometric response. The ILMCT will drop, while the ILLCT could increase due to ligand–metal ion complexation resulting in an increase in 2D ratiometric ILLCT/ILMCT

response. The detection limit of Hg^{2+} ion sensing employing LMOFs has been reported to be in the order of magnitude equal to nM level [64, 68]. Simultaneously, variation in the compound's photo luminescent radiance intensity occurred owing to shifting of electronic cloud from compound to Hg^{2+} ions resulted due to communication of Hg^{2+} ions and functional-ligand, particularly nitrogen donors, residing zinc-LMOF demonstrated ligand rooted radiance while concentrating the connection between mechanism response and structure signal. Although, efficient fabrication of potential Zn^{2+}-LMOFs due to its dissolution in H_2O and photo-durability of the structure are demanded while reproducibility of Zn^{2+}-LMOFs depend on specified functional ligands. The LOD up to level of pM were noticed for gold nanocomposites@UiO-66 [69] and DSM@7 [70], built on MOF. In addition, KSV value for Eu^{3+}@post-improved UiO-66 approached to μM level. Appropriate incorporation of enclosed guest compounds inside porous MOF, employs MOF-supported composite to recognize Hg^{2+} ions proficiently nonetheless, percolation of such kind of sensors must be thoroughly analyzed for practical implications.

3.2. Detection of Al^{3+} ions

Al^{3+} ions in high amount not only affects the well-being of humans but also can cause serious damage to the human body since it is not a scarce constituent essential for humans. This is a reduction in the haste with which Al^{3+} ions are detected. Many efforts have been made to detect Al^{3+} ions using LMOFs and several methodologies have been used in this line. The sensors extinguishing framework of emissive LMOFs resulting in host-signal alteration in response generation and signal transduction are termed as sacrificial sensors. The bonding of organic-ligand and Al^{3+} ions supports various redundant reaction procedures. Intending to recognize Al^{3+} ions, Singha et al. [71] applied 3,5-diamino-1,2,4-triazole (DATZ) and 4,4'-oxybis(benzoic acid) (H_2OBA) to synthesize $[Co(OBA)(DATZ)_{0.5}(H_2O)]$, a triazole-supported (d)-LMOF. Aromatic

ligands attached with metal ions underwent intra-ligand π^*-n and π^*- π^* electronic transitions instigating λ_{max} around 407 nm while the excitation wavelength was 283 nm. In comparison to preliminary emission, translocation of λ_{max} approximately 24 nm with a signal intensification multiple of 6.3 was noticed when [Co (OBA) $(DATZ)_{0.5}(H_2O)$] ((d)-LMOF) was implemented for ion identification, however, displayed insignificant variation in the presence of contrasting metal ions. The attachment of free N-atoms constituent of triazole-ligand (-NH-) and Al^{3+} ions supplied a source for signal-transduction discriminatively. Other metal ions interact with free amine groups via Lewis acid-base interactions, whereas Al^{3+} ions can subtract an H^+ from the NH group of the triazole ring and create triazolate with the amine groups (NH_2) acting as Lewis basic sites due to their high charge-to-size ratio. The blue shift in PL emission peak of frameworks is caused by electrostatic interaction between Al^{3+} ions and the triazolate ring. Furthermore, triazolate production enhances the overall electron density on DATZ, resulting in turn-on luminescence behavior. Because of the limited possibility of forming a triazolate ring in acidic conditions, the results reveal a 2.8 times enhancement that is approximately 3 times less than the value obtained in the initial pure aqueous medium. Based on the strength of architectural uniqueness, revocable pathway and discriminative identification of Al^{3+} ions, it was recommended as an excellent instance of chemical communication betwixt compound and metal ions. Additionally, the maximum LOD was found to be remarkably at high-level in comparison with [Co (OBA) $(DATZ)_{0.5}(H_2O)$] that was observed with a detection limit of 57.6 μg/L. Al^{3+} ions showed LOD of 7.6 mM and 200 μg/L for drinkable H_2O, as suggested by Environmental Protection Agency. Thus, considering it an excellent instance for the appropriate detection limit of renewable and discriminative sensors by slowing down. With intention of preparing [{Cd_2(syn-dftpmcp) (1,3-

380 $BDC)_2\}0.5DMF.H_2O]_n$, Li et al [72] applied post synthesis photo-dimerization process, while
381 (syn-dftpmcp stands for syn-3,4,12,13-tetrakis(4-pyridyl)-8,17-bisfluoro-1,2,9,10-diethano[2.2]
382 metacyclophane). The results of metal ions detection in CH_3CN demonstrate that in the presence
383 of 1 mM/L Al^{3+} ions solution, PL emission of framework is fully quenched with an LOD of 183
384 μg/L.

385 **3.2. More s-block and d-block metal ions**

386 The identification of metal ions such as Zn^{2+}, Ru^{2+}, Tl^{2+}, Pb^{2+}, Ni^{2+}, Mn^{2+}, Mg^{2+}, In^{3+}, Ga^{3+}, Fe^{2+},
387 Cr^{3+}, Co^{2+}, Cd^{2+}, Ca^{2+}, Bi^{3+}, Ba^{2+} and Ag^{+} using LMOFs in comparison to previously reported
388 Fe^{3+}, Cr^{3+}, Cu^{2+}, Al^{3+} and Hg^{2+} ions are limited. In addition, such metal ions could be detected
389 with strategies like mechanism response and structure signal, used to implied for redundant metal
390 ions [15-17, 73, 74]. With intention of favorable probing of Pd^{2+} ions, although, the metal ions are
391 redundantly detected following linker metal ions bonding. As a result, greater research into the
392 detection of these metal ions by LMOFs is required due to the environmental threats and harms
393 that these metal ions cause to humans, as well as the development of information about LMOFs in
394 metal ions detection.

395 **3.3. Detection of metal ions from lanthanide series**

396 Unlike the non-radiative d-d transitions in (d)-LMOFs, the f-f transitions in Ln^{3+} ions are radiative
397 if Ln^{3+} ions centers are effectively sensitized through the antenna effect of the organic ligand and
398 the LMREnT process occurs. Depending upon the unique emission maxima of Ln^{3+} ions, enhanced
399 photoluminescence results in proficient LMREnT. Succeeding post-synthesizing Ln^{3+}@MOF-
400 composites, the fundamental factor leading to sensitize Ln^{3+} ions, probing metal ions and emissive
401 character of (f)-LMOFs was supposed to be REnT. Furthermore, the metal ions linking,
402 exchanging cation, configuration breakdown and overlapping manners that are responsible for 1-

dimensional improvement or diminishing of λ_{max} of transduced signal, adopted by (f)-LMOFs employed to sense metal ions. On account of proficient MOF-to- Ln^{3+}-REnT, 1-dimensional turn on the character of specific max of Ln^{3+} ions would be responsible for signal generation after application MOFs to sense Ln^{3+} ions. Because of this reason, Sm^{3+}, Dy^{3+}, Tb^{3+} and Eu^{3+} ions were scrutinized out of Ln^{3+} ions series. With the application of UV light, colorimetric recognition and 1-dimensional turn-on stimulation could be observed concurrently. As mentioned above, the color variation in MOF to Ln^{3+} ions could be observed bare eye under UV radiation source unveiling their sensitivity, e.g., Sm^{3+} ions showed orange, Dy^{3+} ions displayed blue, Tb^{3+} ions were detected with green and Eu^{3+} ions were observed with red color. The appearance shade of sensing agent alters after interaction of MOFs and Ln^{3+} ions such as Eu^{3+} ions show red color [75], Tb^{3+} ions give green [76], Dy^{3+} ions exhibit blue [77] and Sm^{3+} ions unveil orange color [77]. On the other hand, fabrication of Ln^{3+}@MOF-composites has been widely administered for the identification of varied samples following an efficient approach of sensitizing Ln^{3+} ions. Free functional-ligands co-ordinational manner, inter-change of anions from a porous framework with cations and pores impregnation with Ln^{3+} ions are the most practiced procedures for preparation of Ln^{3+}@MOF-composites for sensitizing Ln^{3+} ions and application of MOFs for Ln^{3+} ions identification. Comprehensively, high proficiency has been acquired with furnishing suitable factors for sensing and identification of Ln^{3+} ions [77].

4. Nanocomposite based optical sensors

The fluorescent nanosensors have been placed in fascinating class of molecular devices for the detection of various heavy metals in the environment. Various organic dyes such as rhodamine, fluorescein and cyanine are being utilized as fluorescent probes in the sensors. Although, a limited excitation spectrum, little signals, low absorption coefficients, less stability and photo bleaching

426 are associated disadvantages [78]. During the excitation process, the dyes exhibit robust phototoxic
427 impacts to create ROS. The basic simple principle of fluorescence sensors is constructed upon
428 particular interaction between the target analyte (metal ion) and detection component
429 (nanomaterial) to initiate alterations in the fluorescence features of nanomaterial [79]. Recently by
430 employing the different nanomaterials the fluorescence sensors have been developed with
431 enhanced selectivity and sensitivity along with nanocomposite synthesis and functionalization
432 with linkers which may be organic. Nanomaterials improved the identification range, on-site
433 identification potential, stability and also efficient performance of fluorescent based sensors [80].
434 The biomolecules existing on nanomaterial surface help binding of the analyte. The NM-metal
435 ions interactions are commonly concerned with direct fluorescent quenching or energy
436 transference phenomena (FRET, PET, NSET) that lead to the detection of analyte [4, 11, 81].
437 Many fluorescent nanomaterials such as MOFs, polymer dots, carbon quantum dots (CQDs),
438 semiconductor quantum dabs (QDs), silver nanoclusters (AgNCs), gold (AuNCs), up-conversion
439 NPs (UCNPs), and metallic NPs explored for metal ions sensors development.

440 **4.1. Metal NPs and CNTs based sensors**

441 The employment of various nanoparticles (UCNPs, metallic nanoparticles etc.) in fluorescent
442 sensors for the identification of heavy metal ions has attained more attraction because of high bio-
443 compatibility, great specificity, facile synthesis, functionalization of surface and optical properties
444 [50, 82]. Features associated with metallic nanoparticles made them ideal for the development of
445 fluorescent probes with a potential optical array [83]. For the identification of Pb^{2+} ions, many
446 fluorescent nanoparticles have attained attention. For example, in the existence of Pb^{2+} ions, the
447 CuNPs templated with poly-thymine (poly-T) displayed quenching [84]. With great selectivity
448 against other various metal particles in ideal conditions, the nanosensor exhibited a LOD of 0.4

449 nM along with a fast identification time (~10 min). This process proved authenticated with tap
450 H_2O along with a recovery of 99.1%.
451 Similarly, label free procedure established by employing the DNA template CuNPs as fluorescent
452 nano-probes for the identification of Pb^{2+} ions [85]. During the NPs synthesis, it was demonstrated
453 that CuNPs were stabilized by dsDNA encased by Cu^{2+} ions. Metallophilic reactions resulted
454 between Cu^{2+} and Pb^{2+} by the addition of Pb^{2+} ions existing at CuNP surfaces, in this manner
455 inducing fluorescence quenching. With the enhancing Pb^{2+} ions concentration within a range of 5-
456 100 nM (LOD = 5 nM), the fluorescence intensity of NPs reduced. Further, biosynthesized silver
457 nanoparticles were used as fluorescent nano-probes for the advancement of turn-on type Pb^{2+} ions
458 sensors in water [86]. Moreover, functionalized silver nanoparticles with the organic compounds
459 served as an excellent sensing site for metal ions identification. For instance, silver nanoparticles
460 that are modified with catechin are utilized for the formation of a more specific fluorescent Pb^{2+}
461 ions sensor [87]. The presence of hydroxyl moieties in catechin initiate the reduction of gold
462 chloride ($AuCl_4^-$) ions to produce gold-based nanoparticles. However, on the introduction of Pb^{2+}
463 ions to the matrix, the complexes of Pb^{2+}-Au and Pb^{2+}-catechin were being developed on the gold
464 nanoparticles surface because of electron rich hydroxyl moieties and this enhanced the catalytic
465 potential of gold-based nanoparticles similar to peroxidases. For instance, in the existence of H_2O_2
466 the oxidized amplex ultra red (AUR) probe exhibited the robust intensity of the fluorescence. A
467 linear relation between AUR intensity and Pb^{2+} ions concentration with LOD of 1.5 nM was
468 exhibited by H_2O_2-Catechin-AUR-AuNP probe. Gold based nanoparticles (AuNPs) were being
469 utilized in association with Brilliant Cresyl Blue (BCB) dye for the formation of a FRET-based
470 fluorescent nano-sensor in the near infrared range [88]. The restoration of BCB dye fluorescence
471 occurs because of dye molecules detachment from the gold-based nanoparticles that occurs due to

the addition of the Pb^{2+} ions. At optimum conditions, the chelation reaction happened between glutathione capped gold nanoparticles and Pb^{2+} ions. The Pb^{2+} ions concentration could be identified by the nanosensor in the range of 0.16 to 2.1 ng/mL. The nanosensor showed great sensitivity and insignificant interference because of absorbance in NIR region. Gold nanoparticles have been employed as significant fluorescence quencher in NSET method because they have capability to multiply the transfer of energy process [89, 90].

For the optical identification of metallic ions (Pb^{2+} and Hg^{2+}), the gold nanoparticles are used in the conjugation with aptamers. The linear relationship between the concentration of these ions and fluorescence intensity was exhibited in the range of 10 pM to 1 μM. Furthermore, the LOD of 27 pM for Pb^{2+} and 51 pM for Hg^{2+} was calculated by using the equation 3σ/slope in 10 mM sodium phosphate buffer. On the other hand, the LOD for Pb^{2+} and Hg^{2+} in human blood serum was as low as 128 pM and 121 pM respectively [91]. To enhance the selectivity and sensitivity of the fluorescent nanosensors, the employment of up-conversion nanoparticles (UCNPs) doped with the metal/lanthanide ions attracts a great amount of attention during the last decades. Up-conversion nanoparticles have displayed excellent photo-luminescent characteristics through the following mechanism of dual/multi-photon. Further, these have capability to transform longer wavelengths to shorter wavelength fluorescent emissions [92]. In FRET-based Pb^{2+} ions nanosensor, the up-conversion nanoparticles of $NaYF_4$ functionalized with the ethylene-imine polymer and gold nanoparticles capped with the 11-mercaptoundecanoic acid (MUA) utilized as acceptors and donors respectively [93]. The mechanism of identification is based upon ions chelation that detached Up-conversion NPs from gold nanoparticles in the existence of the Pb^{2+} ions which results in donor fluorescence restoration. With the LOD of 20 nM, the linear identification limit for the established sensor was described as between 0.5 to 10 μM.

Based on gold nano rods (AuNRs) and $NaYF_4$: Yb, Ho up-conversion nanoparticles, the dual FRET based apta sensor was being formed for the identification of the metal ions [94]. Firstly, the up-conversion nanoparticles improved with amino ($-NH_2$) moiety associated aptamers through covalently bond and gold nanorods functionalized with thiol-modified corresponding DNA sequences of the Pb^{2+} ions specific DNAzymes. The up-conversion fluorescence (green and red) of UCNPs was quenched because of instantaneous overlapping between absorption spectra of gold nanoparticles and fluorescence emission spectra of up-conversion nanoparticles. Up-conversion fluorescence was restored by the introduction of the Pb^{2+} ions to the matrix, because of the development of G-quadruplex structure between the Pb^{2+} ions and aptamers. Between Pb^{2+} ions concentration and nanoparticles fluorescence intensity, the enhanced linear relationship was observed within the range of 0.1-100 nM (LOD = 50 pM). By utilizing the human blood serum samples and the environmentally polluted food samples, the nanosensor was examined with a restoration value between 96 and 110.6% [94]. Recently for Pb^{2+} ions identification, the $NaYF_4/Yb^{3+/}Tm^{3+}$ UCNPs were used as FRET donors while TGA capped CdTe QDs employed as FRET acceptors in nanosensors [95]. The advanced system identified Pb^{2+} ions in human serum with great capability to overcome the auto-fluorescence of serum with LOD of 80 nm. For the identification of Pb^{2+} ions, the fluorescent probes such as AuNCs, AuNRs and AgNCs utilization are the point of interest these days [96-99]. For example, based on fluorescence quenching the glutathione functionalized gold nanorods have been reported for selective Pb^{2+} ions sensing [100]. The nanosensor exhibited great sensitivity in an array of 5 nM to 5 mM with LOD of 2 nM. In the same way as a ratiometric fluorescent probe for the identification of Pb^{2+} ions, a hybrid of SiNPs connected with AuNCs/QDs was utilized [101]. Based on ratiometric intensity (I_{520}/I_{620}) with various Pb^{2+} ions concentrations from 0 to 250 nM (LOD = 3.5 nM) the fluorescence quenching

capability of the probe was calculated. Polyvinyl alcohol (PVA) strips coated with AuNC/QD hybrid structures are employed for the identification of Pb^{2+} ions in mineral water, seawater, ground water and tap water. A metal ion identification range of 0.1 μM was shown by the solid sensor strip [101]. Similarly, for the identification of Pb^{2+} ions in living cells the glutathione (GSH) capped fluorescent silver nanoclusters (AgNCs) have been reported [102]. The identification was based on quenching (fluorescence) because of the coordination connections between Pb^{2+} ions and carboxy/amino moieties existing on GSH-AgNCs (LOD = 0.2 nM). Silver nanoclusters have been templated with the PS_2.M-DNA to form a Pb^{2+} ions nano-biosensor [102]. Fluorescence was enhanced by the introduction of Pb^{2+} ions into the sensor via G-quadruplex development from aptamer-DNA. The two dark AgNC-DNAs situated at 3' and 5' terminals exhibited fluorescence and these were produced due to alteration in DNA-aptamer conformation. With LOD of 3 nM, the higher sensitivity was shown by the nanosensor in the range of 5 to 50 nM. For selectively identifying the Pb^{2+} ions, recently the gold nanoclusters capped with the MPA and GSH have been produced by employing core-etching and ligand change reaction [103]. Big clusters of non-luminescent gold nanoclusters have been produced due to aggregation of gold nanoclusters as well as the interaction between Pb^{2+} ion and thiol moiety present on surface of gold nanoclusters. In natural drinking water, the sensor has LOD of 10 nM. In the identification of metal ions, the CNTs also described as an outstanding fluorescence quencher other than metal nanoparticles [104]. For example, for formation of multi-plexed aptamer metal ions identification system the fluorescence quenching features of multi-walled carbon nanotubes (MWCNTs) were being utilized [105] and system exhibited the LOD of 20 nM. For higher sensitive Pb^{2+} ions sensing, the CNTs functionalized by ATTO-647 N/aptamers have been developed [106]. With LOD of 0.42 nM, the developed aptasensor exhibited significant sensing of Pb^{2+} ions in tap H_2O and in serum samples.

Fluorescent nanosensors behaved as amazing sensing tool for practical applications due to designed nanomaterials.

4.2. Carbon quantum dots (CQDs) based sensors

A very attractive class of fluorescent nanomaterials is the carbon quantum dots (CQDs)/carbon dots (CDs) with many amazing characteristics such as the existence of numerous functionalities, cost-effective, facile preparation, tunable emissions, strong photoluminescence, the potential of surface functionalization, bio-compatibility, good photo-stability and very good water solubility [107]. In sensing various kinds of heavy metal ions like Zn^{2+}, Cr^{6+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Fe^{3+}, Se^{4+}, As^{3+}, Hg^{2+} and Pb^{2+} ions the CQDs are being employed extensively [108, 109]. Biocompatible and non-toxic CQDs are obtained from natural carbon resources [110]. The general detecting mechanisms of CQD sensors are fluorescence quenching, fluorescence activation, PET, FRET and inside filter effect (Fig. 6).

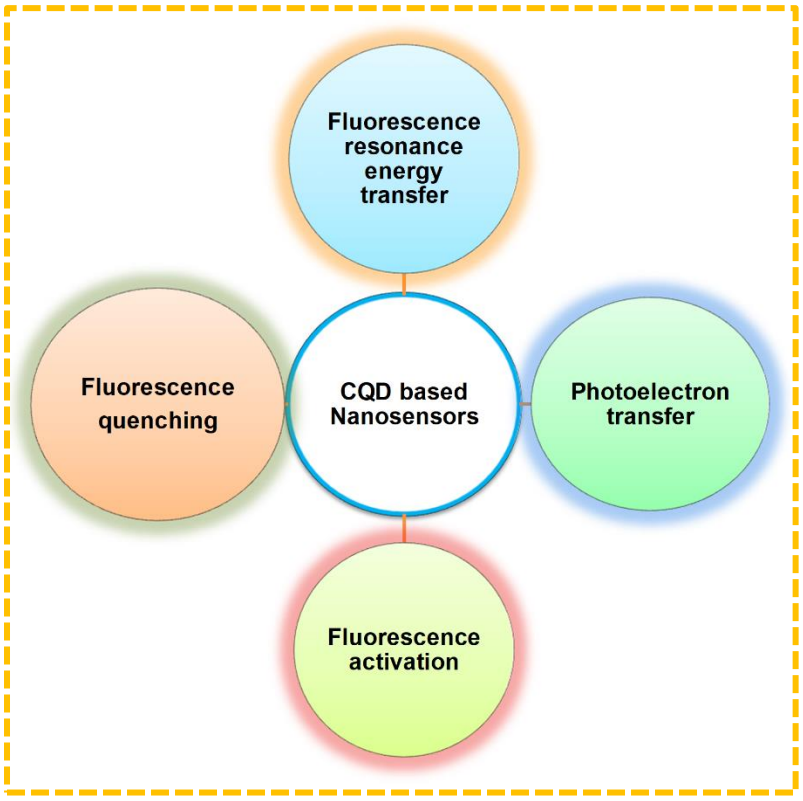

Fig.6. General Mechanistic approach of CQDs based nanosensors for sensing of metal ions.

For example, in chocolate, H_2O soluble fluorescent CQDs are produced by single step hydro-thermal reaction [111]. The prepared CQDs based sensor is employed for the detection of Pb^{2+} ions. Great sensitivity was exhibited by nanosensor because of fluorescent quenching that was based on an interaction between Pb^{2+} ions and hydroxyl moieties upon the CQDs. For Pb^{2+} ions detection, the CQDs prepared from the *Osmium Sanctum* were also utilized [112]. Fluorescence of CQDs is greatly quenched in the presence of Pb^{2+} ions because of electron transference (non-radiative) in which amine moiety existing on surfaces of CQD interacted with Pb^{2+} ions (empty d-orbitals). In the same manner, the preparation of nitrogen-doped CQDs was carried out by employing the *Lantana camera* berries (as a source of carbon) and for the doping agent, EDTA was used [113]. In human serum and real water samples, the CQDs (QY= 33.15%) were being utilized as an amazing sensing agent for the identification of Pb^{2+} ions with the sensing limit from 0 to 200 nM with 9.6 nM LOD. The *Gingko biloba* leaf extracts were utilized for the derivation of flavonoid doped CQDs these were used for the development of a Pb^{2+} ions sensor [114]. Flavonoid glycosides present on the surface of CQDs were being specifically bonded by Pb^{2+} ions and this led to fluorescence quenching. With a LOD of 55 μM, the Pb^{2+} ions detected by the nanosensor were within the 1-20 nM range. Through dipole-dipole force and hydrogen bonding, the agarose hydrogel was further used for flavonoid-CQDs doping to develop a detecting system. With 12.89 nM LOD the gel slices were utilized for the removal and identification of Pb^{2+} ions [114]. For fluorescence and colorimetric-based Pb^{2+} ions sensing in water samples, the fabrication of the CQDs with table sugar was carried out [114]. Turbidimeter was employed to quantify the Pb^{2+} ions concentration with excellent selectivity (LOD = 14 μg/L) that was close to the permissible limit of Pb^{2+} ions in drinking H_2O (15 μg/L). Similarly, the dextrose ager also known as biological media was employed for the carbon nano-rods preparations through microwave heating for the

578 formation of an effective lead sensor [115]. The multicolor fluorescence was exhibited by the
579 multicolor CQDs and water-soluble CQDs. Pb^{2+} ions developed a complex by coordinating with
580 hydroxyl and carboxylic moieties existing upon CQDs surface that initiate the fluorescence
581 quenching via PET mechanism (with LOD 0.73 nM and 1.1 nM in tap water samples and river
582 water samples respectively [116]. On the cellulose paper strips the CQDs were additionally
583 embedded that exhibited the identification limit of 106 μM [115, 116]. For Pb^{2+} ions sensing in
584 aqueous solution, the chemically prepared CQDs were also utilized. Nitrogen doped CQDs (N-
585 CQDs) were synthesized using glycerol and EDTA (under microwave radiations exhibiting LOD
586 of 0.1-6 μM [117]. Fluorescent CQDs were synthesized using bovine serum albumin protein
587 through single step method (LOD = 5.05 μM) [118]. Conjugation of N-CQDs was done with
588 magnetic NPs (Fe_3O_4 nanoparticles) for the identification and adsorption of Pb^{2+} ions [118]. For
589 the pre-concentration and solid-phase extraction of Pb^{2+} ions from vegetative samples and H_2O
590 samples, N-CQD/ Fe_3O_4 NP hybrid adsorbent material was utilized. The presence of functional
591 moieties (hydroxyl, carboxylic and C-O-C-) on CQDs permitted great Pb^{2+} ions adsorption during
592 extraction with an identification range of 0.3 to 300 μg/L [39]. Moreover, for the development of
593 a turn-off/on Pb^{2+} ions sensor the CQDs were also utilized. Thus, for the instantaneous
594 identification of pyrophosphate (PPi) and Pb^{2+} ions, highly fluorescent and water-soluble CQDs
595 were obtained from kerosene soot [119]. The interaction of Pb^{2+} ions with carboxyl moieties
596 existing on the surface of CQDs lead to reduce the CQDs intensity of fluorescence. By
597 incorporation of PPi in the system, fluorescence was regained because of the great binding
598 capability to Pb^{2+} ions than CQDs. With LOD of 2 nM, the Pb^{2+} ions were identified in the range
599 of 0.5 to 11 μM. By utilizing the sodium-citrate and poly-acrylamide (precursors) the blue
600 fluorescent CQDs were prepared for the advancement of "turn-off/on" Pb^{2+} ions sensor with a

601 detection limit of 4.6 nM [120]. For the development of "turn-off/on type" Pb^{2+} ions sensor, boron
602 doped CQDs are reported [121]. The chelation between Pb^{2+} ions and oxygen atoms existing on
603 the surface of CQD forms complex (non-fluorescent) with DL of 25 to 250 μM. The N-CQDs
604 acquired from pyrolysis of citric acid and ethanol-amine have been demonstrated for the formation
605 of "turn-on" type Pb^{2+} ions sensor [122]. Initially, due to interaction (electrostatic) between the
606 carboxyl moieties of PAAs and amino groups of CQDs (range 0-1.67 mM and LOD of 22.8 μM),
607 the fluorescence of immobilized CQDs (at λ_{max} 430 nm) was quenched. For the identification of
608 bio-molecules, analytes and metals, CQD based ratiometric fluorescent method have been
609 employed [70]. Through solvothermal process, the multiemissive CQD hybrids were synthesized
610 from bamboo leaves [70]. Hybrids of CQDs were synthesized in existence of sodium carbonate to
611 acquire triple emissive CQDs at a single wavelength of 400 nm. The Pb^{2+} ions interacted with
612 flavonoid moieties existing on surface of CQD with quenching fluorescence of CQDs @ 493 nm
613 and improved signal @ 653 nm. The fluorescence response plotted against Pb^{2+} ions concentration
614 to get detection range from 0.6 to 800 nM (with LOD of 0.14 nM). In another study, CQDs were
615 produced by utilizing the glutathione and formamide under microwave method by employing a
616 ratiometric fluorescent sensing system [123]. The CQDs (QY 6.49%) exhibited fluorescence and
617 absorption both in blue and red spectral regions at the same time. The interactions between the
618 Pb^{2+} ions and surface groups (-COOH, C=N, C=S) of the CQDs are driven to such fluorescence
619 quenching. With a LOD of 37.1 nM, the double fluorescent CQDs exhibited a greater sensitivity
620 within linear range (1-961 nM). For FRET-based identification of Pb^{2+} ions, another ratiometric
621 fluorescent sensor was created utilizing amino capped CQDs and the GSH-functionalized gold
622 nanoclusters (AuNCs) [124]. The CQDs (positively charged) served as energy donor and gold
623 nanoclusters (negatively charged) employed as energy acceptors and both of these were utilized

as FRET pair in research work. When excited at a wavelength of 380 nm the fluorescent probe exhibited double crests at 440 and 565 nm. The introduction of Pb^{2+} ions enhanced the gold nanoclusters fluorescence while this did not affect the CQDs. This happened because thiolated gold nanoclusters exhibited photo-luminescence on their aggregation [125]. Within the limit of 2 to 60 μM and with an LOD of 0.5 μM, the created ratiometric sensor showed a direct relationship between Pb^{2+} ions concentration and probe ratiometric intensity (I_{565}/I_{440}). In view of these improvements and a broad ubiquity of CQDs as a lead detecting material, it could be concluded that environment friendly CQD-based sensing probes will coordinate with simpler readout frameworks and imaging helped quantification strategies in the future.

4.3. Nanocomposites for colorimetric responses

Nanoparticles such as gold, silver and lead have peroxidase mimetic potential and the gathering of these nanoparticles with graphene can increase their stability, in addition, provide them with excellent catalytic potential. By utilizing this characteristic, several sensors for heavy metal ions have been proposed. It was evident that GO-AuNP nanohybrids with peroxidase type potential would distinguish between the single and double-stranded deoxy-ribonucleic acid (DNA) and then Pb^{2+}, Hg^{2+} ions could be colorimetrically identified based on the metal ion activated DNA conformation development [126]. According to a research report, the existence of Hg^{2+} could increase and improve the peroxidase mimetic potential of reduced graphene oxide/poly-ethyleneimine/palladium-nanoparticles (rGO/PEI/Pd) nanohybrids enhancing the oxidation and color variation of 3,3',5,5'-tetra-methylbenzidine in solution and recognizing selective identification of Hg^{2+} ions with LOD of 0.39 nM (Fig. 7) [127].

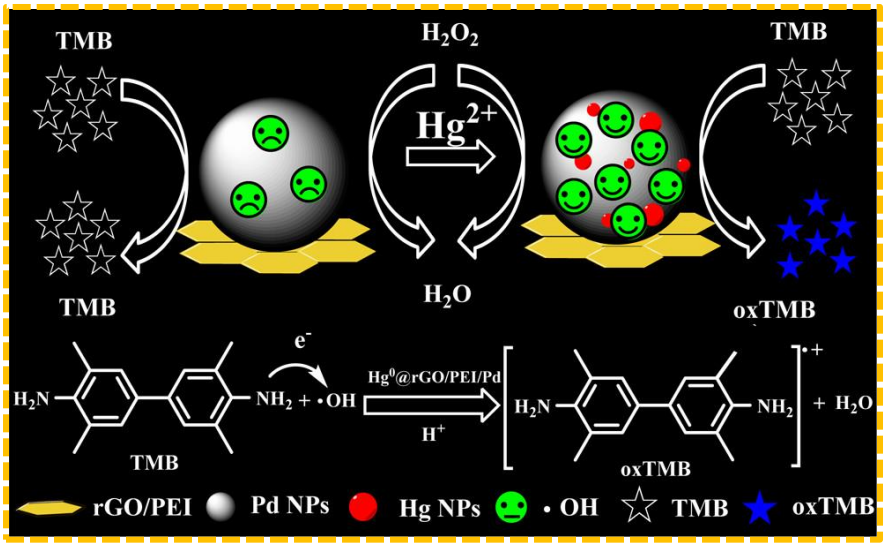

Fig. 7. Mercury-enhanced peroxidase-like activity of rGO/PEI/Pd nanohybrids and reaction principle. This figure is obtained with permission from Ref. [127].

Zhi and coworkers [128] made graphene-doped MoS_2 aerogels to support Au/Fe_3O_4 nano-particles. Fe_3O_4 nanoparticles bestowed magnetic features to aerogels. The prepared nanohybrid materials facilitate facile reusability and recovery of catalyst. Further, the detection was supported by the addition of gold nanoparticles in an aqueous medium. The formed Hg^{2+} ions contained aerogel that stimulated peroxidase mimetic potential. In addition to the per-oxidase mimetic potential, upon introduction of Hg^{2+} ions the direct solution color change of the nanocomposites has also been referred to as the detection of Hg^{2+} ions. By following a simple one-pot oxidation-reduction reaction, Yan and his colleagues [129] prepared multi-functional graphene gold nanocomposites (G-AuNPs). The formed G-AuNPs initiate a colorimetric change upon introduction of Hg^{2+} ions from purple red to brown in the presence of ascorbic acid. These colorimetric changes owe the formation of an amalgam of AuNPs enabling the naked eye identification of Hg^{2+} ions.

4.4. Nanocomposites for fluorescent detection

Graphene oxide and graphene have been used (as substrate) for loading of fluorophore through direct assembling of fluorescent nanoparticles or by employing biomolecules to capture the fluorophores. The simultaneous removal and identification of Hg^{2+} ions was carried out using rGO-Fe_3O_4 functionalized with Hg^{2+} ions specific T-DNA [130]. In another study, the detection of Hg^{2+} ions with double-gold nanoclusters/graphene oxide (D-GNCs/GO) has been reported via electrostatic interactions. where D-GNCs enhance the detection sensitivity and graphene oxide can stimulate the rate of reaction [131]. Graphene oxide decorated with AuNCs@BSA is employed for the identification and isolation of Hg^{2+} ions based on the metal binding characteristic of AuNCs@BSA nanofibers and large surface area of graphene oxide. It was assumed that the high separation effectiveness of the hybrid membrane can be ascribed to the uncommon Hg^{2+}-Au^{+} interactions, Hg^{2+}-cysteine residue binding, and the hybrid membrane (Fig. 8) [132]. Liu et al. [133] adjusted graphene oxide with Ag-In-Zn-S quantum dabs (QDs). The addition of Cu^{2+} ions would initiate the accumulation of QDs and consequent fluorescence quenching can be utilized for Cu^{2+} ions assurance.

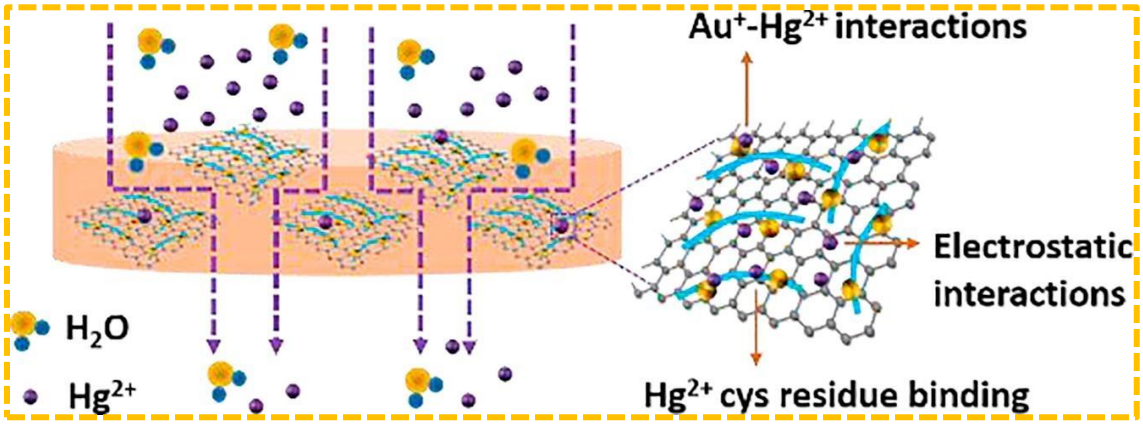

Fig. 8. Adsorption mechanism in the stacked sheets of GO-AuNCs@BSA nanofibers hybrid membrane. This figure was obtained with permission from Ref. [132].

4.5. Nanocomposites as fluorescence quenchers

679 Dye-labelled ssDNA by hydrophobic and π–π interactions may be well adsorbed by graphene
680 oxide and at the same time quench the fluorescence of dyes resonance by FRET, whereas dsDNA
681 or other DNAs are not able to bind to the surface of graphene oxide. These features made graphene
682 oxide an attractive and efficient DNA based fluorescent sensing system for the identification of
683 heavy metal ions. FRET/shell-insulated metal nanoparticle surface-enhanced fluorescence
684 spectroscopy (FRET/SIMNSEF) protocol having graphene oxide and anisotropic shell-insulated
685 metallic nanoparticles (SIMNs) demonstrated for the sensing of Hg^{2+} ions by T-rich ssDNA
686 functionalization. While the absence of Hg^{2+} ions, fluorophore-labelled ssDNA adorned on SIMNs
687 adsorb on the surface of graphene oxide and thus the fluorescence could be quenched by the FRET.
688 DNA hairpin framework formation is due to THg^{2+}-T coordination. Furthermore, the decreased
689 interaction between the graphene oxide and DNA provides ultimate fluorescence restoration and
690 further the surface enhanced fluorescence (SEF) effect increase and amplify the fluorescence
691 signal, realizing the sensitive identification of Hg^{2+} ions [134]. Two hairpin probes and a helper
692 DNA have been designed and these could be adsorbed on graphene oxide to quench the
693 fluorescence of the label. The hybridization chain reactions (HCRs) between the two hairpin
694 probes started through the Hg^{2+} ions employing the helper DNA by T- Hg^{2+}-T coordination
695 chemistry. The dsDNA products were released from the graphene oxide and the fluorescence was
696 restored. The methodology can be applied in sensitive Hg^{2+} ion sensing with a LOD of 0.3 nM
697 [135].
698 Similarly, Hg^{2+} (Ag^{+}, Pb^{2+}) ions sensing platforms have been constructed based on fluorescence
699 variation because of conformation DNA development on combining with Hg^{2+} (Ag^{+}, Pb^{2+}) ions to
700 create the T- Hg^{2+}-T (C-Ag^{+}-C, Pb^{2+}-G-quadruplex) base pairs [136-138]. The sensing platforms
701 for Hg^{2+} and Pb^{2+} ions identification have been proposed on basis of quenching nanoparticles

fluorescence [139, 140]. As a linker to bridge graphene oxide and GQDs another distinctive technique utilized Grich DNA and after that to initiate the formation of G-quadruplex the Pb^{2+} ions were utilized. Leading to the shortening of the distance between graphene oxide and GQDs leading to an alteration within the chain length, in this way fluorescence quenching was observed in GQDs and this happened due to energy transfer between graphene oxide and GQDs [141]. Metal ion specific DNAzymes have been utilized for the construction of the detecting platform. Liu and his colleagues [142] reported the Cu^{2+} ions dependent DNAzyme having a 30-FAM-developed Cu-Sub and a Cu-Enzyme can be gathered with graphene, resulting in close proximity of fluorophore to the surface of graphene to assist the complete quenching. The self-gathered graphene DNAzyme configuration disturbed by the proximity of Cu^{2+} ions would cleave the DNA substrate hence discharging FAM-labeled DNA strand to produce increased Cu^{2+} ions concentration dependent fluorescence signals. FAM-labeled were also replaced by fluorophore [143]. For the examination of Pb^{2+} ions, the DNAzyme principle was implemented [144]. To create an inflexible structure with little ssDNA circles they utilized Pb^{2+} ions dependent 8-17 DNAzymes to hybridize with the Cy3-labeled substrate that might not tie effectively to graphene oxide, and in this way, the fluorescence of Cy3 might not be quenched. Upon Pb^{2+} ions addition, the Cy3- labelled part was discharged and 17S substrate strand was cleaved, leading to the strong quenching of the fluorescence flag by graphene oxide. The obtained results were controversial [145]. Different fluorescence responses in reference [145] may be due to various lengths and configurations of DNAzyme-substrates and different affinities of discharged fragments to graphene/graphene oxide. Molecular beacon (MB) having fluorophore and a quencher in near vicinity with quenched fluorescence and furthermore the graphene oxide adsorption can reduce the back-ground fluorescence. The Cu^{2+} ions and H_2O_2 existence may break the molecular beacons into small

portions that can be released from surface of graphene oxide which restores the Cu^{2+} ions dependent fluorescence [146].

4.6. Probing through fluorescent nanoclusters

Surface-layer of rGO was passivated and its FL intensified after improvement with T following SN^2 methodology, demonstrated by Dinda and coworkers [147]. Grounding on Thymine- Hg^{2+} -T communication, Hg^{2+} ions recognition has been tripped by applying the thermally reduced graphene oxide as a fluorescence detector. On the account of elevated bonding fascination of Hg^{2+} and I^- ions, the I^- ions could be identified with greater ease. A remarkable refurbishment and revamping in the fluorescence of graphene was proposed by Fu and coworker [148] that in the existence of $S_2O_3^{2-}$ and $HOCH_2CH_2SH$, Pb^{2+} ions increased the percolating speed of gold-NPs that in-turn was produced quenching of graphene fluorescence intensity. Moreover, mineral water and tap water specimens are also supplied with the same sensor for estimating Pb^{2+} ions. Ag^+ and Hg^{2+} ions sensing has also been acquired with the nearness of these ions transferring electrons between these ions and graphene oxide, like customary fluorescence -NPs e.g., semiconducting quantum dots. The fluorescence quenching owing to electron transfer among heavy metal ions and graphene oxide succeeding evolution of double-stranded DNA with a hairpin appearance that emerged after particular Hg^{2+}/Ag^+ ions adhering to single-stranded DNA (T-rich/C-rich) preceding its functionalization on the surface of graphene oxide [148, 149]. For the manufacturing of nano compounds with dual radiance characteristics, semiconducting quantum dots were aided via GO displaying efficient fluorescence and were introduced by Li et *al*. [149]. It is advantageous in discriminative and responsive detection of Cu^+ ions [149]. Advantageously, responsive and discriminative ascertainment of Cu^+ ions has been achieved through observing its effect on NCs

fluorescence red glow turning blue and red colored fluorescence emission of quantum dots got quenched while graphene oxide underwent no change in fluorescence shade.

5. Differentiation between orthodox sensors and nano-sensors

Inorganic precursors with non-poisonous, cost-effective and bio-suitable in nature are used to prepare nanomaterials supported probs in contrast to traditionally employed probs. Virtually, such probes have been fascinated because of facile synthetic procedures and potential implications, inexpensiveness and increased LOD. For modelling and preparation of optical sensors, NMs are used as excellent translating-section due to their distinguishing characteristics. Furthermore, optical characteristics of NMs were arrayed by target-initiated aggregation/anti-aggregation and surface improvement [32, 52]. In addition, optical sensors of nano substances were analyzed with smaller sized ligands/macro-biomolecules being the identification module. Particular and distinguished sensing of heavy metal ions was also possible with the detection section that furnishes the target specimen with unique biological and chemical interactions. Moreover, swift qualitative/quantitative sensing of heavy metals with greater selectivity in comparison to colorimetric detectors has been achieved using luminescence-based nanoparticles. On contrary, some of the disadvantages related to the aqueous detections and biologically active metal ions detection were noticed on the rounds of poor water solubility, toxicity and inappropriateness of orthodox photoluminescent organic dyes like organic fluorophores and emissive conjugated-polymers [150]. For apprehending organic luminescence, a detailed overview of the structure and synthetic pathways of the compound must be known in comparison to luminescent nanoparticles. Photobleaching of organic dyes could happen even with facile observation and elevated susceptibility. The photo-bleaching of organic chromophores is repressed by Raman sensors. However, electromagnetic amplification causes Raman scattering remarkably effective when poor

efficiency was faced. Therefore, SERES and LOD could proficiently be improved with standardization of constitution, volume and configuration of plasmonic nano-structures [151]. Furthermore, the implementation of nanomaterials as sensing modalities has greatly improved the sensing abilities of chemosensors. In an aqueous solution, the distinctive identification of Cu^{2+} and Hg^{2+} ions were achieved through immobilization of emissive dipeptidyl chemosensor (DPN) over silicon nanoparticles generating SiNPs@DPN by Chung and his coworkers [91]. Conjugation of MSiNPs with DPN remarkably enhanced LOD up to 96 nM for Hg^{2+} ions. Metallic ions in lower amounts were ascribed to nanoparticles triggering signal enlargement. Likewise, 0.768 μM LOD was observed for discerning Cu^{2+} ions under chemosensor radiant of rhodamine B [152]. Nevertheless, an upgraded LOD of less than 0.3 mg/L and boosted response for probing Cu^{2+} ions in the solution state was exhibited by surface modified MSNPs with rhodamine implanted through covalent bonds. Noticeable implications are discerned for lab on chip technology and bioimaging owing to efficient regenerative ability and resilience of hybrid-substance. Macro-biomolecules and micro-molecular ligands were employed probing agent for contrasting organic fluorescent nanosensors and chemosensors.

6. Conclusion and future prospects

The necessity of unique tools for real-time detection of diverse water contaminants is generally recognized around the world. This review offered a critical appraisal of recent advances in a real-time monitoring system, based on the fluorescent, luminescence and colorimetric detection methods. The focus of this review ass to present the advancement in nanomaterial-based nanosensors for sensing heavy metal ions in aqueous matrices with enhanced selectivity, efficacy and sensitivity. Sensors exhibited better sensitivity and selectivity with the incorporation of nanomaterials. In a comparison of conventional sensors, nanomaterial-based sensors are found

preferable because of facile synthesis, lower LOD values and cost-effectiveness in various practical applications. Despite significant advancements and developments, the recognition of heavy metal ions by these nanostructures still faces significant developmental problems related to their suitability in real-world samples such as biological and raw water samples. The weak self-stability of nanostructures must be addressed to meet the requirement for heavy metal ions monitoring in complex matrices such as biological samples, wastewater and seawater samples. As a result, new stable nanomaterials must be designed and developed, necessitating the use of novel modification techniques for enhanced functionalization. Additionally, in designing the nanomaterial-based sensors, selectivity must be addressed by selecting suitable binding sites such as specific biological macromolecules or small organic molecules which selectively binds the analytes of major concern. Finally, combining nano-systems with other technologies such as microfluidic or paper chips, as well as test strips, holds a lot of potential for the creation of portable devices that can detect heavy metal ions on a commercial or industrial scale. In conclusion, combining nano-systems with other technologies such as paper chips, microfluidic as well as test strips, holds a lot of potential for the creation of portable devices that can detect heavy metal ions on an industrial or commercial scale

Acknowledgments

The representative Universities or institutes are thankfully acknowledged for providing literature services.

Conflict of interest disclosure

The representative authors have no conflict of interest to disclose in any capacity, either competing or financial.

References

[1] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: a review, Journal of Environmental Management, 92 (2011) 407-418.
[2] T. Rasheed, F. Nabeel, C. Li, Y. Zhang, Rhodol assisted alternating copolymer based chromogenic vesicles for the aqueous detection and quantification of hydrazine via switch-on strategy, Journal of Molecular Liquids, 274 (2019) 461-469.
[3] T. Rasheed, F. Nabeel, K. Rizwan, M. Bilal, T. Hussain, S.A. Shehzad, Conjugated supramolecular architectures as state-of-the-art materials in detection and remedial measures of nitro based compounds: a review, TrAC Trends in Analytical Chemistry, 129 (2020) 115958.
[4] T. Rasheed, F. Nabeel, S. Shafi, Chromogenic vesicles for aqueous detection and quantification of Hg^{2+}/Cu^{2+} in real water samples, Journal of Molecular Liquids, 282 (2019) 489-498.
[5] T. Rasheed, F. Nabeel, S. Shafi, M. Bilal, K. Rizwan, Block copolymer self-assembly mediated aggregation induced emission for selective recognition of picric acid, Journal of Molecular Liquids, 296 (2019) 111966.
[6] T.H. Zhi-lin Hou, Cai-yun Cai, T. Resheed, C.Yu, Y.Zhou,, D.-y. Yan, Polymer vesicle sensor through the self-assembly of hyperbranched polymeric ionic liquids for the detection of SO_2 derivatives, Chinese Journal of Polymer Science, 35 (2017) 602−610.
[7] V. Poornima, V. Alexandar, S. Iswariya, P.T. Perumal, T.S. Uma, Gold nanoparticle-based nanosystems for the colorimetric detection of Hg^{2+} ion contamination in the environment, RSC Advances, 6 (2016) 46711-46722.
[8] I. Ugulu, Determination of heavy metal accumulation in plant samples by spectrometric techniques in Turkey, Applied Spectroscopy Reviews, 50 (2015) 113-151.
[9] M.S. Gustin, D. Hou, F.M.G. Tack, the term "heavy metal(s)": history, current debate, and future use, Science of the Total Environment, 789 (2021) 147951.
[10] K. Karim, S. Guha, R. Beni, Comparative analysis of water quality disparities in the United states in relation to heavy metals and biological contaminants, Water, 12 (2020) 967.
[11] T. Rasheed, M. Bilal, F. Nabeel, H.M. Iqbal, C. Li, Y. Zhou, Fluorescent sensor based models for the detection of environmentally-related toxic heavy metals, Science of the Total Environment, 615 (2018) 476-485.
[12] T. Rasheed, A.A. Hassan, F. Kausar, F. Sher, M. Bilal, H.M. Iqbal, Carbon nanotubes assisted analytical detection–Sensing/delivery cues for environmental and biomedical monitoring, TrAC Trends in Analytical Chemistry, 132 (2020) 116066.
[13] T. Rasheed, C. Li, M. Bilal, C. Yu, H.M. Iqbal, Potentially toxic elements and environmentally-related pollutants recognition using colorimetric and ratiometric fluorescent probes, Science of the Total Environment, 640 (2018) 174-193.
[14] T. Rasheed, C. Li, F. Nabeel, W. Huang, Y. Zhou, Self-assembly of alternating copolymer vesicles for the highly selective, sensitive and visual detection and quantification of aqueous Hg^{2+}, Chemical Engineering Journal, 358 (2019) 101-109.
[15] T. Rasheed, C. Li, F. Nabeel, M. Qi, Y. Zhang, C. Yu, Real-time probing of mercury using an efficient "turn-on" strategy with potential as in-field mapping kit and in live cell imaging, New Journal of Chemistry, 42 (2018) 10940-10946.
[16] T. Rasheed, F. Nabeel, M. Adeel, K. Rizwan, M. Bilal, H.M. Iqbal, Carbon nanotubes-based cues: a pathway to future sensing and detection of hazardous pollutants, Journal of Molecular Liquids, 292 (2019) 111425.
[17] T. Rasheed, F. Nabeel, C. Li, M. Bilal, Rhodamine-assisted fluorescent strategy for the sensitive and selective in-field mapping of environmental pollutant Hg(II) with potential bioimaging, Journal of Luminescence, 208 (2019) 519-526.
[18] M. Arora, B. Kiran, S. Rani, A. Rani, B. Kaur, N. Mittal, Heavy metal accumulation in vegetables irrigated with water from different sources, Food Chemistry, 111 (2008) 811-815.
[19] J. Briffa, E. Sinagra, R. Blundell, Heavy metal pollution in the environment and their toxicological effects on humans, Heliyon, 6 (2020) e04691.

[20] B. Kaur, R. Srivastava, B. Satpati, Ultratrace detection of toxic heavy metal ions found in water bodies using hydroxyapatite supported nanocrystalline ZSM-5 modified electrodes, New Journal of Chemistry, 39 (2015) 5137-5149.
[21] X. Yuan, M.I. Setyawati, A.S. Tan, C.N. Ong, D.T. Leong, J. Xie, Highly luminescent silver nanoclusters with tunable emissions: cyclic reduction–decomposition synthesis and antimicrobial properties, NPG Asia Materials, 5 (2013) e39-e39.
[22] C.V. Hoang, M. Oyama, O. Saito, M. Aono, T. Nagao, Monitoring the presence of ionic mercury in environmental water by plasmon-enhanced infrared spectroscopy, Scientific Reports, 3 (2013) 1-6.
[23] M. Li, H. Gou, I. Al-Ogaidi, N. Wu, Nanostructured sensors for detection of heavy metals: a review, ACS Sustainable Chemistry & Engineering, 1, (2013), 713−723
[24] S. Yu, H. Tang, D. Zhang, S. Wang, M. Qiu, G. Song, D. Fu, B. Hu, X. Wang, MXenes as emerging nanomaterials in water purification and environmental remediation, Science of The Total Environment, (2021) 152280.
[25] S. Yu, H. Pang, S. Huang, H. Tang, S. Wang, M. Qiu, Z. Chen, H. Yang, G. Song, D. Fu, Recent advances in metal-organic framework membranes for water treatment: A review, Science of The Total Environment, 800 (2021) 149662.
[26] S. Zhang, J. Wang, Y. Zhang, J. Ma, L. Huang, S. Yu, L. Chen, G. Song, M. Qiu, X. Wang, Applications of water-stable metal-organic frameworks in the removal of water pollutants: A review, Environmental Pollution, 291 (2021) 118076.
[27] E. Singh, M. Meyyappan, H.S. Nalwa, Flexible graphene-based wearable gas and chemical sensors, ACS Applied Materials & Interfaces, 9 (2017) 34544-34586.
[28] S.K. Krishnan, E. Singh, P. Singh, M. Meyyappan, H.S. Nalwa, A review on graphene-based nanocomposites for electrochemical and fluorescent biosensors, RSC Advances, 9 (2019) 8778-8881.
[29] S.B. Borah, T. Bora, S. Baruah, J. Dutta, Heavy metal ion sensing in water using surface plasmon resonance of metallic nanostructures, Groundwater for Sustainable Development, 1 (2015) 1-11.
[30] P. Gruber, M.P. Marques, N. Szita, T. Mayr, Integration and application of optical chemical sensors in microbioreactors, Lab on a Chip, 17 (2017) 2693-2712.
[31] H.H. Qazi, A.B. Mohammad, M. Akram, Recent progress in optical chemical sensors, Sensors, 12 (2012) 16522-16556.
[32] Y. Ding, S. Wang, J. Li, L. Chen, Nanomaterial-based optical sensors for mercury ions, TrAC Trends in Analytical Chemistry, 82 (2016) 175-190.
[33] I. Buryakov, T. Buryakov, V. Matsaev, Optical chemical sensors for the detection of explosives and associated substances, Journal of Analytical Chemistry, 69 (2014) 616-631.
[34] F. Nabeel, T. Rasheed, Rhodol-conjugated polymersome sensor for visual and highly-sensitive detection of hydrazine in aqueous media, Journal of Hazardous Materials, 388 (2020) 121757.
[35] F. Nabeel, T. Rasheed, M.F. Mahmood, S.U.-D. Khan, Hyperbranched copolymer based photoluminescent vesicular probe conjugated with tetraphenylethene: Synthesis, aggregation-induced emission and explosive detection, Journal of Molecular Liquids, 308 (2020) 113034.
[36] Z. Wang, L. Zhang, K. Zhang, Y. Lu, J. Chen, S. Wang, B. Hu, X. Wang, Application of carbon dots and their composite materials for the detection and removal of radioactive ions: A review, Chemosphere, 287 (2022) 132313.
[37] J. Li, J.-J. Zhu, Quantum dots for fluorescent biosensing and bio-imaging applications, Analyst, 138 (2013) 2506-2515.
[38] Y.Y. Wang, X. Xiang, R. Yan, Y. Liu, F.L. Jiang, Förster resonance energy transfer from quantum dots to rhodamine B as mediated by a cationic surfactant: a thermodynamic perspective, The Journal of Physical Chemistry C, 122 (2018) 1148-1157.
[39] J. Ju, W. Chen, Synthesis of highly fluorescent nitrogen-doped graphene quantum dots for sensitive, label-free detection of Fe (III) in aqueous media, Biosensors and Bioelectronics, 58 (2014) 219-225.
[40] S. Li, Y. Li, J. Cao, J. Zhu, L. Fan, X. Li, Sulfur-doped graphene quantum dots as a novel fluorescent probe for highly selective and sensitive detection of Fe^{3+}, Analytical Chemistry, 86 (2014) 10201-10207.

[41] J. Wang, C. Jiang, X. Wang, L. Wang, A. Chen, J. Hu, Z. Luo, Fabrication of an "ion-imprinting" dual-emission quantum dot nanohybrid for selective fluorescence turn-on and ratiometric detection of cadmium ions, Analyst, 141 (2016) 5886-5892.
[42] J. Liu, G. Lv, W. Gu, Z. Li, A. Tang, L. Mei, A novel luminescence probe based on layered double hydroxides loaded with quantum dots for simultaneous detection of heavy metal ions in water, Journal of Materials Chemistry C, 5 (2017) 5024-5030.
[43] R. Zhang, W. Chen, Nitrogen-doped carbon quantum dots: facile synthesis and application as a "turn-off" fluorescent probe for detection of Hg^{2+} ions, Biosensors and Bioelectronics, 55 (2014) 83-90.
[44] B. Paramanik, S. Bhattacharyya, A. Patra, Detection of Hg^{2+} and F^{-} ions by using fluorescence switching of quantum dots in an Au-cluster–CdTe QD nanocomposite, Chemistry–A European Journal, 19 (2013) 5980-5987.
[45] D. Chen, H. Feng, J. Li, Graphene oxide: preparation, functionalization, and electrochemical applications, Chemical Reviews, 112 (2012) 6027-6053.
[46] Y.-L. Zhang, L. Wang, H.-C. Zhang, Y. Liu, H.-Y. Wang, Z.-H. Kang, S.-T. Lee, Graphitic carbon quantum dots as a fluorescent sensing platform for highly efficient detection of Fe^{3+} ions, RSC Advances, 3 (2013) 3733-3738.
[47] X. Ran, H. Sun, F. Pu, J. Ren, X. Qu, Ag nanoparticle-decorated graphene quantum dots for label-free, rapid and sensitive detection of Ag^{+} and biothiols, Chemical Communications, 49 (2013) 1079-1081.
[48] Y.-C. Lu, J. Chen, A.-J. Wang, N. Bao, J.-J. Feng, W. Wang, L. Shao, Facile synthesis of oxygen and sulfur co-doped graphitic carbon nitride fluorescent quantum dots and their application for mercury (II) detection and bioimaging, Journal of Materials Chemistry C, 3 (2015) 73-78.
[49] J. Chang, G. Zhou, E.R. Christensen, R. Heideman, J. Chen, Graphene-based sensors for detection of heavy metals in water: a review, Analytical and Bioanalytical Chemistry, 406 (2014) 3957-3975.
[50] J.R. Choi, D. M. Shin, H. Song, D. Lee, K. Kim, Current achievements of nanoparticle applications in developing optical sensing and imaging techniques, Nano Convergence, 3 (2016) 1-13.
[51] E. Singh, H. Nalwa, Nanomaterial-based flexible and multifunctional sensors, in, American Scientific Publishers, Los Angeles, 2019.
[52] M. Sabela, S. Balme, M. Bechelany, J.M. Janot, K. Bisetty, A review of gold and silver nanoparticle-based colorimetric sensing assays, Advanced Engineering Materials, 19 (2017) 1700270.
[53] Z. Ansari, S.S. Singha, A. Saha, K. Sen, Hassle free synthesis of nanodimensional Ni, Cu and Zn sulfides for spectral sensing of Hg, Cd and Pb: A comparative study, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 176 (2017) 67-78.
[54] J. Li, Q. Wang, Z. Guo, H. Ma, Y. Zhang, B. Wang, D. Bin, Q. Wei, Highly selective fluorescent chemosensor for detection of Fe^{3+} based on Fe_3O_4@ZnO, Scientific Reports, 6 (2016) 1-8.
[55] A. Shahat, M.R. Awual, M. Naushad, Functional ligand anchored nanomaterial based facial adsorbent for cobalt (II) detection and removal from water samples, Chemical Engineering Journal, 271 (2015) 155-163.
[56] M.R. Awual, M.M. Hasan, G.E. Eldesoky, M.A. Khaleque, M.M. Rahman, M. Naushad, Facile mercury detection and removal from aqueous media involving ligand impregnated conjugate nanomaterials, Chemical Engineering Journal, 290 (2016) 243-251.
[57] Y. Cao, W. Wu, S. Wang, H. Peng, X. Hu, Y. Yu, Monolayer gC_3N_4 fluorescent sensor for sensitive and selective colorimetric detection of silver ion from aqueous samples, Journal of Fluorescence, 26 (2016) 739-744.
[58] A. Kaur, G. Kaur, A. Singh, N. Singh, N. Kaur, Polyamine based ratiometric fluorescent chemosensor for strontium metal ion in aqueous medium: application in tap water, river water, and in oral care, ACS Sustainable Chemistry & Engineering, 4 (2016) 94-101.
[59] H.-R. Fu, Y. Zhao, T. Xie, M.-L. Han, L.-F. Ma, S.-Q. Zang, Stable dye-encapsulated indium–organic framework as dual-emitting sensor for the detection of Hg^{2+}/$Cr_2O_7^{2-}$ and a wide range of nitro-compounds, Journal of Materials Chemistry C, 6 (2018) 6440-6448.

[60] X.-Y. Xu, B. Yan, Fabrication and application of a ratiometric and colorimetric fluorescent probe for Hg^{2+} based on dual-emissive metal–organic framework hybrids with carbon dots and Eu^{3+}, Journal of Materials Chemistry C, 4 (2016) 1543-1549.
[61] P. Samanta, A.V. Desai, S. Sharma, P. Chandra, S.K. Ghosh, Selective recognition of Hg^{2+} ion in water by a functionalized metal–Organic framework (MOF) based chemodosimeter, Inorganic Chemistry, 57 (2018) 2360-2364.
[62] S.A.A. Razavi, M.Y. Masoomi, A. Morsali, Double solvent sensing method for improving sensitivity and accuracy of Hg (II) detection based on different signal transduction of a tetrazine-functionalized pillared metal–organic framework, Inorganic Chemistry, 56 (2017) 9646-9652.
[63] A. Pankajakshan, D. Kuznetsov, S. Mandal, Ultrasensitive detection of Hg (II) ions in aqueous medium using zinc-based metal–organic framework, Inorganic Chemistry, 58 (2019) 1377-1381.
[64] P. Wu, Y. Liu, Y. Liu, J. Wang, Y. Li, W. Liu, J. Wang, Cadmium-based metal–organic framework as a highly selective and sensitive ratiometric luminescent sensor for mercury (II), Inorganic Chemistry, 54 (2015) 11046-11048.
[65] Z. Xiaoxiong, Z. Wenjun, L. Cuiliu, Q. Xiaohong, Z. Chengyu, Eu^{3+} postdoped UIO-66-type metal–organic framework as a luminescent sensor for Hg^{2+} detection in aqueous media, Inorganic Chemistry, 58 (2019) 3910-3915.
[66] H. Tan, B. Liu, Y. Chen, Lanthanide coordination polymer nanoparticles for sensing of mercury (II) by photoinduced electron transfer, ACS Nano, 6 (2012) 10505-10511.
[67] Z.-J. Wang, L.-J. Han, X.-J. Gao, H.-G. Zheng, Three Cd (II) MOFs with different functional groups: selective CO_2 capture and metal ions detection, Inorganic Chemistry, 57 (2018) 5232-5239.
[68] A. Shahat, H.M. Hassan, H.M. Azzazy, Optical metal-organic framework sensor for selective discrimination of some toxic metal ions in water, Analytica Chimica Acta, 793 (2013) 90-98.
[69] S. Govindaraju, P. Puthiaraj, M.-H. Lee, K. Yun, Photoluminescent AuNCs@UiO-66 for ultrasensitive detection of mercury in water samples, ACS Omega, 3 (2018) 12052-12059.
[70] H. Zhai, Y. Bai, J. Qin, F. Feng, Colorimetric and ratiometric fluorescence dual-mode sensing of glucose based on carbon quantum dots and potential UV/fluorescence of o-diaminobenzene, Sensors, 19 (2019) 674.
[71] D.K. Singha, P. Mahata, Highly selective and sensitive luminescence turn-on-based sensing of Al^{3+} ions in aqueous medium using a MOF with free functional sites, Inorganic Chemistry, 54 (2015) 6373-6379.
[72] W.-X. Li, J.-H. Gu, H.-X. Li, M. Dai, D.J. Young, H.-Y. Li, J.-P. Lang, Post-synthetic modification of a two-dimensional metal–organic framework via photodimerization enables highly selective luminescent sensing of aluminum (III), Inorganic Chemistry, 57 (2018) 13453-13460.
[73] T. Rasheed, F. Nabeel, Luminescent metal-organic frameworks as potential sensory materials for various environmental toxic agents, Coordination Chemistry Reviews, 401 (2019) 213065.
[74] T. Rasheed, F. Nabeel, M. Adeel, M. Bilal, H.M. Iqbal, "Turn-on" fluorescent sensor-based probing of toxic Hg(II) and Cu(II) with potential intracellular monitoring, Biocatalysis and Agricultural Biotechnology, 17 (2019) 696-701.
[75] Y. Gao, X. Zhang, W. Sun, Z. Liu, A robust microporous metal–organic framework as a highly selective and sensitive, instantaneous and colorimetric sensor for Eu^{3+} ions, Dalton Transactions, 44 (2015) 1845-1849.
[76] F.Y. Yi, J.P. Li, D. Wu, Z.M. Sun, A series of multifunctional metal–organic frameworks showing excellent luminescent sensing, sensitization, and adsorbent abilities, Chemistry–A European Journal, 21 (2015) 11475-11482.
[77] J. An, C.M. Shade, D.A. Chengelis-Czegan, S. Petoud, N.L. Rosi, Zinc-adeninate metal− organic framework for aqueous encapsulation and sensitization of near-infrared and visible emitting lanthanide cations, Journal of the American Chemical Society, 133 (2011) 1220-1223.
[78] W. Gong, P. Das, S. Samanta, J. Xiong, W. Pan, Z. Gu, J. Zhang, J. Qu, Z. Yang, Redefining the photo-stability of common fluorophores with triplet state quenchers: mechanistic insights and recent updates, Chemical Communications, 55 (2019) 8695-8704.

[79] X. Luo, Y. Han, X. Chen, W. Tang, T. Yue, Z. Li, Carbon dots derived fluorescent nanosensors as versatile tools for food quality and safety assessment: A review, Trends in Food Science & Technology, 95 (2020) 149-161.
[80] N. Bhardwaj, S.K. Bhardwaj, M.K. Nayak, J. Mehta, K.-H. Kim, A. Deep, Fluorescent nanobiosensors for the targeted detection of foodborne bacteria, TrAC Trends in Analytical Chemistry, 97 (2017) 120-135.
[81] J. Shi, F. Tian, J. Lyu, M. Yang, Nanoparticle based fluorescence resonance energy transfer (FRET) for biosensing applications, Journal of Materials Chemistry B, 3 (2015) 6989-7005.
[82] B. Gu, Q. Zhang, Recent advances on functionalized upconversion nanoparticles for detection of small molecules and ions in biosystems, Advanced Science, 5 (2018) 1700609.
[83] J. Zhang, F. Cheng, J. Li, J.-J. Zhu, Y. Lu, Fluorescent nanoprobes for sensing and imaging of metal ions: Recent advances and future perspectives, Nano Today, 11 (2016) 309-329.
[84] L. Ou, X. Li, H. Liu, L. Li, X. Chu, Poly (thymine)-templated fluorescent copper nanoparticles for ultrasensitive label-free detection of lead ion, Analytical Sciences, 30 (2014) 723-727.
[85] J. Chen, J. Liu, Z. Fang, L. Zeng, Random dsDNA-templated formation of copper nanoparticles as novel fluorescence probes for label-free lead ions detection, Chemical Communications, 48 (2012) 1057-1059.
[86] L.E. Silva-De Hoyos, V. Sánchez-Mendieta, A.R. Vilchis-Nestor, M.A. Camacho-López, Biogenic silver nanoparticles as sensors of Cu^{2+} and Pb^{2+} in aqueous solutions, Universal Journal of Materials Science, 5 (2017) 29-37.
[87] Y.-S. Wu, F.-F. Huang, Y.-W. Lin, Fluorescent detection of lead in environmental water and urine samples using enzyme mimics of catechin-synthesized Au nanoparticles, ACS Applied Materials & Interfaces, 5 (2013) 1503-1509.
[88] S. Wang, J. Sun, F. Gao, A turn-on near-infrared fluorescent chemosensor for selective detection of lead ions based on a fluorophore–gold nanoparticle assembly, Analyst, 140 (2015) 4001-4006.
[89] C.J. Breshike, R.A. Riskowski, G.F. Strouse, Leaving forster resonance energy transfer behind: nanometal surface energy transfer predicts the size-enhanced energy coupling between a metal nanoparticle and an emitting dipole, The Journal of Physical Chemistry C, 117 (2013) 23942-23949.
[90] L. Chun, C.-Z. HUANG, Detection of lead ions in water based on the surface energy transfer between gold nanoparticles and fluorescent dyes, Chinese Journal of Analytical Chemistry, 42 (2014) 1195-1198.
[91] C.H. Chung, J.H. Kim, J. Jung, B.H. Chung, Nuclease-resistant DNA aptamer on gold nanoparticles for the simultaneous detection of Pb^{2+} and Hg^{2+} in human serum, Biosensors and Bioelectronics, 41 (2013) 827-832.
[92] G. Chen, H. Qiu, P.N. Prasad, X. Chen, Upconversion nanoparticles: design, nanochemistry, and applications in theranostics, Chemical Reviews, 114 (2014) 5161-5214.
[93] Y. Zhang, L. Wu, Y. Tang, Y. Su, Y. Lv, An upconversion fluorescence based turn-on probe for detecting lead (II) ions, Analytical Methods, 6 (2014) 9073-9077.
[94] S. Wu, N. Duan, Z. Shi, C. Fang, Z. Wang, Dual fluorescence resonance energy transfer assay between tunable upconversion nanoparticles and controlled gold nanoparticles for the simultaneous detection of Pb^{2+} and Hg^{2+}, Talanta, 128 (2014) 327-336.
[95] S. Xu, S. Xu, Y. Zhu, W. Xu, P. Zhou, C. Zhou, B. Dong, H. Song, A novel upconversion, fluorescence resonance energy transfer biosensor (FRET) for sensitive detection of lead ions in human serum, Nanoscale, 6 (2014) 12573-12579.
[96] L. Gong, H. Kuai, S. Ren, X.-H. Zhao, S.-Y. Huan, X.-B. Zhang, W. Tan, Ag nanocluster-based label-free catalytic and molecular beacons for amplified biosensing, Chemical Communications, 51 (2015) 12095-12098.
[97] M. Liu, F. Tang, Z. Yang, J. Xu, X. Yang, Recent progress on gold-nanocluster-based fluorescent probe for environmental analysis and biological sensing, Journal of Analytical Methods in Chemistry, 2019 (2019) https://doi.org/10.1155/2019/1095148.
[98] C. Song, J. Xu, Y. Chen, L. Zhang, Y. Lu, Z. Qing, DNA-templated fluorescent nanoclusters for metal ions detection, Molecules, 24 (2019) 4189.

[99] Y. Yang, A. Han, R. Li, G. Fang, J. Liu, S. Wang, Synthesis of highly fluorescent gold nanoclusters and their use in sensitive analysis of metal ions, Analyst, 142 (2017) 4486-4493.
[100] Z. Yuan, M. Peng, Y. He, E.S. Yeung, Functionalized fluorescent gold nanodots: synthesis and application for Pb^{2+} sensing, Chemical Communications, 47 (2011) 11981-11983.
[101] H. Zhu, T. Yu, H. Xu, K. Zhang, H. Jiang, Z. Zhang, Z. Wang, S. Wang, Fluorescent nanohybrid of gold nanoclusters and quantum dots for visual determination of lead ions, ACS Applied Materials & Interfaces, 6 (2014) 21461-21467.
[102] C. Wang, J. Wu, K. Jiang, M.G. Humphrey, C. Zhang, Stable Ag nanoclusters-based nano-sensors: rapid sonochemical synthesis and detecting Pb^{2+} in living cells, Sensors and Actuators B: Chemical, 238 (2017) 1136-1143.
[103] B. Zhang, C. Wei, Highly sensitive and selective detection of Pb^{2+} using a turn-on fluorescent aptamer DNA silver nanoclusters sensor, Talanta, 182 (2018) 125-130.
[104] C. Li, G. Shi, Carbon nanotube-based fluorescence sensors, Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 19 (2014) 20-34.
[105] S.E. Wang, S. Si, Aptamer biosensing platform based on carbon nanotube long-range energy transfer for sensitive, selective and multicolor fluorescent heavy metal ion analysis, Analytical Methods, 5 (2013) 2947-2953.
[106] S.M. Taghdisi, S.S. Emrani, K. Tabrizian, M. Ramezani, K. Abnous, A.S. Emrani, Ultrasensitive detection of lead (II) based on fluorescent aptamer-functionalized carbon nanotubes, Environmental Toxicology and Pharmacology, 37 (2014) 1236-1242.
[107] Y. Huang, N. He, Q. Kang, D. Shen, X. Wang, Y. Wang, L. Chen, A carbon dot-based fluorescent nanoprobe for the associated detection of iron ions and the determination of the fluctuation of ascorbic acid induced by hypoxia in cells and in vivo, Analyst, 144 (2019) 6609-6616.
[108] P. Devi, P. Rajput, A. Thakur, K.-H. Kim, P. Kumar, Recent advances in carbon quantum dot-based sensing of heavy metals in water, TrAC Trends in Analytical Chemistry, 114 (2019) 171-195.
[109] D. Yoo, Y. Park, B. Cheon, M.-H. Park, Carbon dots as an effective fluorescent sensing platform for metal ion detection, Nanoscale Research Letters, 14 (2019) 1-13.
[110] X. Wang, P. Yang, Q. Feng, T. Meng, J. Wei, C. Xu, J. Han, Green preparation of fluorescent carbon quantum dots from cyanobacteria for biological imaging, Polymers, 11 (2019) 616.
[111] Y. Liu, Q. Zhou, J. Li, M. Lei, X. Yan, Selective and sensitive chemosensor for lead ions using fluorescent carbon dots prepared from chocolate by one-step hydrothermal method, Sensors and Actuators B: Chemical, 237 (2016) 597-604.
[112] A. Kumar, A.R. Chowdhuri, D. Laha, T.K. Mahto, P. Karmakar, S.K. Sahu, Green synthesis of carbon dots from *Ocimum sanctum* for effective fluorescent sensing of Pb^{2+} ions and live cell imaging, Sensors and Actuators B: Chemical, 242 (2017) 679-686.
[113] R. Bandi, R. Dadigala, B.R. Gangapuram, V. Guttena, Green synthesis of highly fluorescent nitrogen–doped carbon dots from *Lantana camara* berries for effective detection of lead (II) and bioimaging, Journal of Photochemistry and Photobiology B: Biology, 178 (2018) 330-338.
[114] J. Xu, X. Jie, F. Xie, H. Yang, W. Wei, Z. Xia, Flavonoid moiety-incorporated carbon dots for ultrasensitive and highly selective fluorescence detection and removal of Pb^{2+}, Nano Research, 11 (2018) 3648-3657.
[115] A. Gupta, N.C. Verma, S. Khan, S. Tiwari, A. Chaudhary, C.K. Nandi, Paper strip based and live cell ultrasensitive lead sensor using carbon dots synthesized from biological media, Sensors and Actuators B: Chemical, 232 (2016) 107-114.
[116] J. Yang, J.-X. Wu, Q.-F. Lü, T.-T. Lin, Facile preparation of lignosulfonate–graphene oxide–polyaniline ternary nanocomposite as an effective adsorbent for Pb (II) ions, ACS Sustainable Chemistry & Engineering, 2 (2014) 1203-1211.
[117] Y. Jiang, Y. Wang, F. Meng, B. Wang, Y. Cheng, C. Zhu, N-doped carbon dots synthesized by rapid microwave irradiation as highly fluorescent probes for Pb^{2+} detection, New Journal of Chemistry, 39 (2015) 3357-3360.

[118] S.S. Wee, Y.H. Ng, S.M. Ng, Synthesis of fluorescent carbon dots via simple acid hydrolysis of bovine serum albumin and its potential as sensitive sensing probe for lead (II) ions, Talanta, 116 (2013) 71-76.
[119] Q. Wang, S. Zhang, H. Ge, G. Tian, N. Cao, Y. Li, A fluorescent turn-off/on method based on carbon dots as fluorescent probes for the sensitive determination of Pb^{2+} and pyrophosphate in an aqueous solution, Sensors and Actuators B: Chemical, 207 (2015) 25-33.
[120] Y. Liu, Q. Zhou, Y. Yuan, Y. Wu, Hydrothermal synthesis of fluorescent carbon dots from sodium citrate and polyacrylamide and their highly selective detection of lead and pyrophosphate, Carbon, 115 (2017) 550-560.
[121] Z.-X. Wang, X.-H. Yu, F. Li, F.-Y. Kong, W.-X. Lv, D.-H. Fan, W. Wang, Preparation of boron-doped carbon dots for fluorometric determination of Pb (II), Cu (II) and pyrophosphate ions, Microchimica Acta, 184 (2017) 4775-4783.
[122] Y. Tian, A. Kelarakis, L. Li, F. Zhao, Y. Wang, W. Wang, Q. Yang, Z. Ye, X. Guo, Facile fluorescence "turn on" sensing of lead ions in water via carbon nanodots immobilized in spherical polyelectrolyte brushes, Frontiers in Chemistry, 6 (2018) 470.
[123] F. Yarur, J.-R. Macairan, R. Naccache, Ratiometric detection of heavy metal ions using fluorescent carbon dots, Environmental Science: Nano, 6 (2019) 1121-1130.
[124] L. Wang, H.-X. Cao, Y.-S. He, C.-G. Pan, T.-K. Sun, X.-Y. Zhang, C.-Y. Wang, G.-X. Liang, Facile preparation of amino-carbon dots/gold nanoclusters FRET ratiometric fluorescent probe for sensing of Pb^{2+}/Cu^{2+}, Sensors and Actuators B: Chemical, 282 (2019) 78-84.
[125] W. Liu, X. Wang, Y. Wang, J. Li, D. Shen, Q. Kang, L. Chen, Ratiometric fluorescence sensor based on dithiothreitol modified carbon dots-gold nanoclusters for the sensitive detection of mercury ions in water samples, Sensors and Actuators B: Chemical, 262 (2018) 810-817.
[126] X. Chen, N. Zhai, J.H. Snyder, Q. Chen, P. Liu, L. Jin, Q. Zheng, F. Lin, J. Hu, H. Zhou, Colorimetric detection of Hg^{2+} and Pb^{2+} based on peroxidase-like activity of graphene oxide–gold nanohybrids, Analytical Methods, 7 (2015) 1951-1957.
[127] S. Zhang, D. Zhang, X. Zhang, D. Shang, Z. Xue, D. Shan, X. Lu, Ultratrace naked-eye colorimetric detection of Hg^{2+} in wastewater and serum utilizing mercury-stimulated peroxidase mimetic activity of reduced graphene oxide-PEI-Pd nanohybrids, Analytical Chemistry, 89 (2017) 3538-3544.
[128] L. Zhi, W. Zuo, F. Chen, B. Wang, 3D MoS_2 composition aerogels as chemosensors and adsorbents for colorimetric detection and high-capacity adsorption of Hg^{2+}, ACS Sustainable Chemistry & Engineering, 4 (2016) 3398-3408.
[129] Z. Yan, H. Xue, K. Berning, Y.-W. Lam, C.-S. Lee, Identification of multifunctional graphene–gold nanocomposite for environment-friendly enriching, separating, and detecting Hg^{2+} simultaneously, ACS Applied Materials & Interfaces, 6 (2014) 22761-22768.
[130] Y. Liu, X. Wang, H. Wu, Reusable DNA-functionalized-graphene for ultrasensitive mercury (II) detection and removal, Biosensors and Bioelectronics, 87 (2017) 129-135.
[131] W. Xiaofei, L. Ruiyi, L. Zaijun, L. Junkang, W. Guangli, G. Zhiguo, Synthesis of double gold nanoclusters/graphene oxide and its application as a new fluorescence probe for Hg^{2+} detection with greatly enhanced sensitivity and rapidity, RSC Advances, 4 (2014) 24978-24985.
[132] X. Yu, W. Liu, X. Deng, S. Yan, Z. Su, Gold nanocluster embedded bovine serum albumin nanofibers-graphene hybrid membranes for the efficient detection and separation of mercury ion, Chemical Engineering Journal, 335 (2018) 176-184.
[133] Y. Liu, M. Deng, X. Tang, T. Zhu, Z. Zang, X. Zeng, S. Han, Luminescent AIZS-GO nanocomposites as fluorescent probe for detecting copper (II) ion, Sensors and Actuators B: Chemical, 233 (2016) 25-30.
[134] L. Kong, J. Wang, G. Zheng, J. Liu, A highly sensitive protocol (FRET/SIMNSEF) for the determination of mercury ions: a unity of fluorescence quenching of graphene and enhancement of nanogold, Chemical Communications, 47 (2011) 10389-10391.
[135] J. Huang, X. Gao, J. Jia, J.-K. Kim, Z. Li, Graphene oxide-based amplified fluorescent biosensor for Hg^{2+} detection through hybridization chain reactions, Analytical Chemistry, 86 (2014) 3209-3215.

[136] J.R. Zhang, W.T. Huang, W.Y. Xie, T. Wen, H.Q. Luo, N.B. Li, Highly sensitive, selective, and rapid fluorescence Hg^{2+} sensor based on DNA duplexes of poly (dT) and graphene oxide, Analyst, 137 (2012) 3300-3305.
[137] K. Zhai, Y. Liu, D. Xiang, G. Guo, T. Wan, H. Hu, Dual color fluorescence quantitative detection of mercury in soil with graphene oxide and dye-labeled nucleic acids, Analytical Methods, 7 (2015) 3827-3832.
[138] S. Pang, S. Liu, X. Su, An ultrasensitive sensing strategy for the detection of lead (II) ions based on the intermolecular G-quadruplex and graphene oxide, Sensors and Actuators B: Chemical, 208 (2015) 415-420.
[139] X. Cui, L. Zhu, J. Wu, Y. Hou, P. Wang, Z. Wang, M. Yang, A fluorescent biosensor based on carbon dots-labeled oligodeoxyribonucleotide and graphene oxide for mercury (II) detection, Biosensors and Bioelectronics, 63 (2015) 506-512.
[140] Z.S. Qian, X.Y. Shan, L.J. Chai, J.R. Chen, H. Feng, A fluorescent nanosensor based on graphene quantum dots–aptamer probe and graphene oxide platform for detection of lead (II) ion, Biosensors and Bioelectronics, 68 (2015) 225-231.
[141] X. Sun, Y. Peng, Y. Lin, L. Cai, F. Li, B. Liu, G-quadruplex formation enhancing energy transfer in self-assembled multilayers and fluorescence recognize for Pb^{2+} ions, Sensors and Actuators B: Chemical, 255 (2018) 2121-2125.
[142] M. Liu, H. Zhao, S. Chen, H. Yu, Y. Zhang, X. Quan, A "turn-on" fluorescent copper biosensor based on DNA cleavage-dependent graphene-quenched DNAzyme, Biosensors and Bioelectronics, 26 (2011) 4111-4116.
[143] M. Liu, H. Zhao, S. Chen, H. Yu, Y. Zhang, X. Quan, Label-free fluorescent detection of Cu (II) ions based on DNA cleavage-dependent graphene-quenched DNAzymes, Chemical Communications, 47 (2011) 7749-7751.
[144] X.-H. Zhao, R.-M. Kong, X.-B. Zhang, H.-M. Meng, W.-N. Liu, W. Tan, G.-L. Shen, R.-Q. Yu, Graphene–DNAzyme based biosensor for amplified fluorescence "turn-on" detection of Pb^{2+} with a high selectivity, Analytical Chemistry, 83 (2011) 5062-5066.
[145] Y. Wen, C. Peng, D. Li, L. Zhuo, S. He, L. Wang, Q. Huang, Q.-H. Xu, C. Fan, Metal ion-modulated graphene-DNAzyme interactions: design of a nanoprobe for fluorescent detection of lead (II) ions with high sensitivity, selectivity and tunable dynamic range, Chemical Communications, 47 (2011) 6278-6280.
[146] J. Huang, Q. Zheng, J.-K. Kim, Z. Li, A molecular beacon and graphene oxide-based fluorescent biosensor for Cu^{2+} detection, Biosensors and Bioelectronics, 43 (2013) 379-383.
[147] D. Dinda, B.K. Shaw, S.K. Saha, Thymine functionalized graphene oxide for fluorescence "turn-off-on" sensing of Hg^{2+} and I^- in aqueous medium, ACS Applied Materials & Interfaces, 7 (2015) 14743-14749.
[148] X. Fu, T. Lou, Z. Chen, M. Lin, W. Feng, L. Chen, "Turn-on" fluorescence detection of lead ions based on accelerated leaching of gold nanoparticles on the surface of graphene, ACS Applied Materials & Interfaces, 4 (2012) 1080-1086.
[149] M. Li, X. Zhou, W. Ding, S. Guo, N. Wu, Fluorescent aptamer-functionalized graphene oxide biosensor for label-free detection of mercury (II), Biosensors and Bioelectronics, 41 (2013) 889-893.
[150] B. Wang, J. Hai, Z. Liu, Q. Wang, Z. Yang, S. Sun, Selective detection of iron (III) by rhodamine-modified Fe_3O_4 nanoparticles, Angewandte Chemie International Edition, 49 (2010) 4576-4579.
[151] M. Li, S.K. Cushing, H. Liang, S. Suri, D. Ma, N. Wu, Plasmonic nanorice antenna on triangle nanoarray for surface-enhanced Raman scattering detection of hepatitis B virus DNA, Analytical Chemistry, 85 (2013) 2072-2078.
[152] Y. Hu, F. Zhao, S. Hu, Y. Dong, D. Li, Z. Su, A novel turn-on colorimetric and fluorescent sensor for Fe^{3+} and its application in living cells, Journal of Photochemistry and Photobiology A: Chemistry, 332 (2017) 351-356.