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REVIEW PAPER

Colorimetric Sensors of Hg^{2+} Ion Based on Functionalized Gold and Silver Nanoparticles

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ABSTRACT

Monitoring the levels of toxic Hg^{2+} metal ions in an aquatic environment is an important issue because this ion can have an adverse effect on human health and the environment. Therefore, the detection of Hg^{2+} ions in water is a very important issue for improving human health and water quality. Metallic nanoparticles such as gold and silver nanoparticles (AuNPs & AgNPs) have received much attention due to their colorimetric properties as well as localized surface plasmon resonance (LSPR) properties. AuNPs and AgNPs can easily change their color (AuNPs: Red to Pink/Blue; AgNPs: Yellow to blue) which is easily discriminated by visual inspection. Functionalization of AuNPs and AgNPs offers an excellent application in many scientific worlds as the choice of ligands/functionalizing groups is of utmost importance for their colloidal stability and function of the nanoparticles. In this review, we have discussed the colorimetric sensors of gold and silver nanoparticles based on the functionalization of organic ligands, polymers, amino acids, and proteins for the detection of Hg^{2+} ions in an aqueous medium.

Keywords: *Colorimetric Sensor, Gold nanoparticles, Silver nanoparticles, Toxic metal ion,* Hg^{2+}

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INTRODUCTION AND BACKGROUND

Heavy or toxic metal ions are mainly contaminated to the environment due to their broad-spectrum application in industry as well as agriculture. Among the several heavy metal ions mercury, cadmium and lead are the most toxic to the human body as well as animals. Other than these three, the human body is also affected by many metal ions including arsenic, chromium, manganese, copper, zinc, etc. even at the minute level of exposure of these metal ions are responsible to cause several diseases to the human body. The list of some toxic metal ions and their biological effects on humans and animals is listed in Table 1.

Among them, mercury is a very well-known toxic metal which is a culprit for several threats to human health and the environment [1]. Mercury contaminates into air, soil, and water due to the production of different sources such as gold production, coal plants, thermometers, barometers, caustic soda, and mercury lamps [2]. Mercury converts itself to methyl mercury and is ready to penetrate itself into the human body through the food chain which may damage the various organs [3-5]. Accumulation of mercury to the human body leads to various cognitive and motor disorders, including Minamata disease [4,6]. Therefore, monitoring of mercury metal ions in water (drinking, sea, lake, etc.) is very essential in terms of improving human health and water quality [7]. Several methods are used for the detection of

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Table 1. List of some toxic metal ions and their biological effects on humans and animals

Toxic metals	Effects in human health	Effects in Animals
Mercury	Tremors, gingivitis, minor psychological changes, acrodynia characterized by pink hands and feet, spontaneous abortion, damage to nervous system, protoplasm Poisoning, Minamata disease	Abnormal reproduction, oxidative stress, damage to cells and tissues, neurochemical changes, Neuro & immune toxic to animals
Cadmium	Renal dysfunction, Lung disease, Lung cancer, Bone defects (Osteomalacia, Osteoporosis), increased blood pressure, kidney damage, bronchitis, gastrointestinal disorder, bone marrow, cancer, Itai–Itai disease	zinc and calcium homeostasis, acute or chronic disease experienced by the cells.
Lead	Mental retardation in children, developmental delay, fatal infant encephalopathy, congenital paralysis, sensor neural deafness and, acute or chronic damage to the nervous system, epilepticus, liver, kidney, gastrointestinal damage	behavioural abnormalities, hearing deficits, neuromuscular weakness, and impaired cognitive functions to the experimental animals
Arsenic	Loss of appetite, gastrointestinal problem, Bronchitis, dermatitis, sometime skin cancer	increases in cytotoxicity, oxidative stress and a decrease of antioxidant enzymes activity
Chromium	Damage to the nervous system, fatigue, irritability	Cr(VI) compounds induced DNA damage, gene mutation, sister chromatid exchange, chromosomal aberrations in a number of targets, in animal cells in vivo
Manganese	Inhalation or contact causes damage to central nervous system, Respiratory Effects, Cardiovascular Effects, Haematological Effects	Failure in development of animal foetuses and brain damage
Copper	Liver and kidney damage, stomach, and intestinal irritation	Hepatic and renal changes most common effects in animals.
Zinc	Zinc fumes have corrosive effect on skin, cause damage to nervous membrane	Severe pathological change occurs in animals such as skin parakeratosis, reduced of growth, general debility, lethargy.

heavy or toxic metal ions which are often based on chromatographic and spectroscopic techniques such as inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), high-performance liquid chromatography (HPLC), electrochemistry and X-ray fluorescence spectroscopy [8-10]. Although these methods are highly sensitive and selective, yet they require highly sophisticated instruments, expensive, time-consuming, non-portable, and unsuitable for on-site analyses. Therefore, low-cost, simple, rapid, portable, and green methods for metal ions detection are still highly desired. Among the several methods, colorimetric methods based on gold and silver nanoparticles is a promising field in the last three decades due to their simplicity, cost-effectiveness, rapid detection as well as low detection limit [11-17]. Gold and silver nanoparticles (AuNPs & AgNPs) based colorimetric sensors are the most convenient due to their surface plasmon resonance (SPR) absorption and changes in their color which can be determined easily by visual inspection as well as UV-Visible spectroscopy [18]. The SPR property largely depends on the size, shape, capping agents/ligands, and inter-particles distances. The choice of ligands or capping agents is solely responsible for the stability of nanoparticles, size, shape as well as properties of the nanoparticles. Thus, functionalization of AuNPs and AgNPs may help for selective recognition of the analytes.

In this article, we have discussed the colorimetric sensors of AuNPs and AgNPs upon functionalization of various organic ligands, amino acid, DNA, protein for colorimetric determination of Hg^{2+} ions.

SYNTHESIS AND FUNCTIONALIZATION OF GOLD NANOPARTICLES (AUNPS)

Procedures for AuNPs

Michael Faraday synthesized colloidal gold hydrogel in 1857 through the reduction of a chloroauric solution by phosphorus dissolved in carbon disulfide [19]. This was the first demonstrated and worldwide accepted colloidal gold synthesis. After almost one century later in1951, gold nanoparticles were synthesized by reduction of chloroauric acid in presence of sodium citrate where sodium citrate acts as a reducing agent as well as a capping agent developed by Turkevich [20]. This is the most widely used method for obtaining AuNPs. In this approach, the required amount of aqueous solution of citrate was added to the boiling water containing $HAuCl_4$ solution where $Au^{3+}$was reduced to metallic Au^0

by changing the color from pale yellow to wine red, indicating the formation of AuNPs. Later, Frens extended the method to control the size of AuNPs by changing the amount of citrate solution concentrations [21]. When the concentration of citrate increases, the corresponding gold size decreases, and vice versa as the citrate adsorbs onto the gold surface through its carboxyl groups with different possible binding modes [22]. The negative charge of citrate provides colloidal stability through electrostatic repulsion and electrostatically coated colloids are well-dispersed in water. Thus, the higher the concentration of citrate will be higher the absorption of citrate onto AuNPs surface resulting to prevent agglomeration and lowering the size of AuNPs. In 1994, an ultra-small size of AuNPs was synthesized by Brust and Schiffrin in the organic phase [23] with the basic concept of a strong interaction between gold and thiol group. The surfactant of tetraethylammonium bromide (TOAB) plays an important role to bring $AuCl^-$ in the organic phase (toluene) from an aqueous phase. Gold ion was reduced by sodium borohydride in presence of dodecanethiol. The method enables one to control the size of AuNPs in the range of 1.5-5 nm by changing the concentration of gold-thiol ratio and reaction conditions such as reaction rate and temperature. The size of AuNPs may be controlled by changing the concentration of gold-thiol ratio as the synergic effect of the strong thiol-gold interactions and van der Waals attractions between the neighboring ligands [24] which helps for controlling the size of AuNPs. The prepared AuNPs are very stable due to strong interactions between gold and thiol groups. Later, other reducing agents were used instead of $NaBH_4$ such as super hydride [25], a glutathione [26] for the synthesis of stable AuNPs using the Brust and Schiffrin [24]. To control the shape of AuNPs, single-step synthesis is a failure. To overcome this limitation, seed growth mediated synthesis is an important process where two steps are generally applied. In the first step, AuNPs seed solution was prepared and then it is added to the 'growth' solution. The growth solution contains $HAuCl_4$, stabilizing and reducing agents. The amount and nature of stabilizing agents and their ratio to Au^{3+} precursor provide to control the size, shape, and surface properties of the seed-growth mediated synthesis [27]. The procedure for the synthesis of the gold nanorods (AuNRs) was reported by Murphy's group using a seed-mediated growth process in presence of ascorbic acid, cetyltrimethylammonium bromide (CTAB) surfactant, and $AgNO_3$. The ascorbic acid reduces $HAuCl_4$ to $HAuCl_2$ followed by the addition of citrate capped AuNPs to the seed solution [28]. In this approach, ascorbic acid reduces Au^+ to Au^0 over AuNP seeds, and structure is directed by CTAB surfactant. El-Sayed's group improved the yield and polydispersity of the AuNRs by replacing the citrate stabilizer of seeds with a stronger stabilizer of CTAB [29] in presence of $AgNO_3$.Other methods were addressed such as photochemical [30], electrochemical [31], sonochemical [32], templates based [33] and galvanic replacement based [34] method for the synthesis of AuNPs. The top-down approach involves the breaking down of the bulk material into nanosized particles and it is used for the synthesis of micron-size particles. These approaches are inherently simpler and depend either on the removal or division of bulk material to produce the desired structure with appropriate properties. The major drawback of the top-down approach is the imperfection of surface structure. There are so many "Top-down" approaches for synthesizing the nanosized particles are photolithography and electron beam lithography [35-36]. AuNPs synthesis and then functionalized by bidentate N-heterocyclic carbene ligands (NHC) reported by Man et al. [37] using a top-down approach. AgNPs have been synthesized using e evaporation–condensation approach and the laser ablation technique [38]. The synthesis of AgNPs by evaporation–condensation through the tube furnace has numerous drawbacks. To overcome this drawback, Jung et al. reported that ceramic heaters can be utilized efficiently in the synthesis of AgNPs with high concentration [39].

Functionalization of Gold Nanoparticles (AuNPs)

Gold nanoparticles are prepared using reducing agents or stabilizing agents. Stabilizing agents play an important role to protect self-aggregation. Turkevich prepared citrate capped AuNPs where citrate acts as a reducing agent as well as stabilizing agent to protect the self-aggregation of AuNPs. But the interaction between citrate O-atom and the surface of Au nanoparticles is very weak and as a result, it can be replaced easily by suitable ligands to prepare functionalized AuNPs. The AuNPs prepared using the Brust-Schiffrin method alkyl thiols such as dodecanethiol, are on their surfaces. The surface of anisotropic AuNPs (nanorods, plates, etc.) is generally covered with surfactant molecules such as CTAB. For biological and chemical applications, these ligands were generally replaced by proper ligands to improve the colloidal stability of the particles and to make the particles water-soluble, biocompatible, and/or specific to a chemical or biological molecule. In other words, for selective or specific recognition of analytes surface functionalization of AuNPs is very essential in terms of biological and sensing application. Due to the strong binding interaction between Au-S and Au-N, many biological and non-biological molecules can cover the whole surface of AuNPs or partial substitution through the electrostatic interaction and covalent interaction [40]. For chemical sensing applications, AuNPs surfaces were modified with various small organic molecules or biological molecules (e. g. aptamers and peptides) which will be discussed later in detail.

SYNTHESIS AND FUNCTIONALIZATION OF SILVER NANOPARTICLES (AGNPS)

Synthesis of Silver Nanoparticles (AgNPs)

AgNPs can be synthesized mainly either physical method or chemical method. The physical method is more advantageous compared to a chemical method as there is no possibility for solvent contamination and nanoparticles are distributed uniformly [41]. But some disadvantages are there during the preparation of AgNPs using a physical method by tube furnace. Here tube furnace requires large space, a lot of time to achieve thermal stability, and consumes a huge amount of energy resulting rise in temperature of the environmental source. AgNPs are also synthesized using laser ablation by bulk metallic solution [42]. The ablation efficiency and characteristics of AgNPs depend upon the many parameters such as the wavelength of laser source on the metallic surface, the duration of laser pulses in the range of nano, pico, and femtosecond regime, the laser fluence, the ablation time duration, and the effective liquid medium, with or without the presence of surfactants [43-45]. The important advantage of this method (ablation) is the nanoparticles could be prepared in absence of any chemical reagents in the solution. Therefore, this technique [46] is most useful for the preparation of pure and uncontaminated metal nanoparticles.

Chemical reduction is the most common technique for the preparation of AgNPs by using organic and inorganic reducing agents. Generally, different reducing agents such as sodium citrate, ascorbate, sodium borohydride ($NaBH_4$), elemental hydrogen, polyol process, Tollens reagent, N, N-dimethylformamide (DMF), and poly (ethylene glycol)-block copolymers are used for the reduction of silver ions (Ag^+) in aqueous or non-aqueous solutions. These reducing agents reduce Ag^+ ion to metallic silver (Ag^0), followed by agglomeration into oligomeric clusters. These clusters eventually lead to the formation of metallic colloidal silver particles [47-49]. Other methods (excluding physical and chemical methods) are also reported for AgNPs preparation such as microemulsion, UV-initiated photoreduction, photoinduced reduction, electrochemical synthetic method, irradiation methods, microwave-assisted synthesis, etc. Uniform and size controllable AgNPs were synthesized using microemulsion techniques. UV-initiated photoreduction is a very simple and cost-effective technique where UV-light was used for the synthesis of AgNPs in presence of citrate, polyvinylpyrrolidone, poly (acrylic acid), and collagen. Huang and Yang [50] produced silver NPs production via photoreduction of silver nitrate in layered inorganic laponite clay suspensions which served as a stabilizing agent for the prevention of NPs aggregation. UV irradiation photoreduction technique was applied using poly (vinyl alcohol) at room temperature where concentrations of both poly (vinyl alcohol) and silver nitrate played a significant role in the growth of the nanorods [51]. The photoinduced or photocatalytic reduction method utilizes to fabricate the AgNPs using various mediums such as cells, emulsion, polymer films, surfactant micelles, glasses, etc. Ghosh and colleagues [52] reported a simple and reproducible UV photo-activation method for the preparation of stable silver NPs in aqueous Triton X-100 (TX-100) where Trixon-100 acts as a stabilizing agent as well as capping agent.

Functionalization of Silver Nanoparticles (AgNPs)

Silver nanoparticles are synthesized by using various stabilizing or protecting agents to prevent self-aggregation in solutions. But for biological and biochemical applications as well as for the applications for sensing and selective recognition of some analytes, it is very important to functionalize the surface of AgNPs. Citrate stabilized AgNPs are weakly bonded due to weak interaction between O-atoms of citrate and the surface of AgNPs. Therefore, replacements of citrate from the surface of AgNPs by various other molecules including

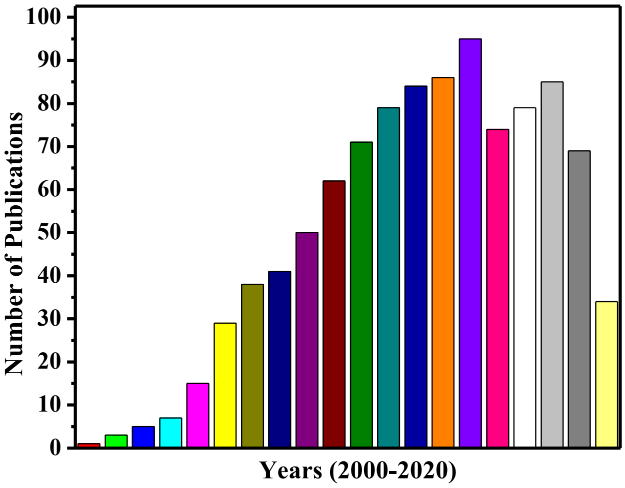

Fig. 1. Year wise statistics for the colorimetric detection of Hg^{2+} ion using functionalized AuNPs (2000-2020, Left to Right).

thiols, amines, polymers, antibodies, and proteins are done easily.

COLORIMETRIC DETECTION OF HG^{2+} USING FUNCTIONALIZED GOLD NANOPARTICLES (AUNPS)

Recently, researchers are involved in the colorimetric detection of metal ions using Gold nanoparticles (AuNPs) because of their inorganic core composition, exhibit strong optical absorption and scattering [53]. Various AuNPs-based colorimetric Chemosensor for detection of Hg^{2+} ion has been proposed and the main focus is drawn to manipulate the AuNPs with different recognition units such as oligonucleotides, DNAzymes, peptides, and proteins, and small thiolate ligands to induce aggregation, thus resulting in a color change. The Year-wise statistics for Hg^{2+} detection using functionalized AuNPs are shown in **Fig. 1.**

Organic Ligands

Amino acid-modified gold nanoparticles are found to be highly sensitive in the detection of mercury ions. Lysine promoted Hg^{2+} detection [54] using AuNPs are shown in **Fig. 2**. Initially, the surface of AuNPs is covered by citrate ions, which are replaced after the addition of Hg^{2+} ions to the AuNPs solution. After the addition of lysine to the Hg^{2+}-capped AuNPs, the color of the AuNP solution immediately changes from red to purple or gray due to the aggregation of AuNPs.The limit of detection of this colorimetric assay is 2.9 nM, which is below the limit value (10 nM) according to U.S. Environmental Protection Agency in drinking water.

A facile colorimetric sensor assay was developed by Denizli et al. [55] using 11-mercaptoundecanoic acid (MUA)-capped gold nanoparticles (AuNPs) and five amino acids (lysine, cysteine, histidine, tyrosine, and arginine) for detection of toxic metal ions (Hg^{2+}, Cd^{2+}, Fe^{3+}, Pb^{2+}, Al^{3+}, Cu^{2+}, and Cr^{3+}) in water. In the amino acids, the presence of various functional groups that can form complexes with AuNPs and MUA regulates the aggregation of MUA-capped AuNPs; it can either enhance or diminish the particle aggregation in presence of toxic metal ions. The ultrasensitive and very selective colorimetric assay has been developed [56] using anisotropic AuNPs where lysine (Lys) and dithiothreitol (DTET) are the aggregations' promotors. The limit of detection was found to be 27 pm and 58 pm for Hg^{2+} in deionized water and tap water. Thymine acetamido ethanethiol (T–SH) capped AuNPs have been used for colorimetric detection of Hg^{2+}. In presence of both T–SH and Hg^{2+}, the aggregation of gold nanoparticles was brought and as a result, the shift of absorption spectrum occurred from 520 nm to 660 nm with a detection limit of 50 nM [57] The detection limit for a mercaptoethyl modified thymine functionalized gold nanoparticle probe had found to be 2.8 nM [58]. L-Cysteine-modified AuNPs had a LOD of 100 nM [59]. Ethanolic 4-amino thiophenol (4-ATP) capped gold AuNPs are used [60] for colorimetric detection of Hg^{2+}. Owing to the strong affinity between the -SH group of 4-ATP

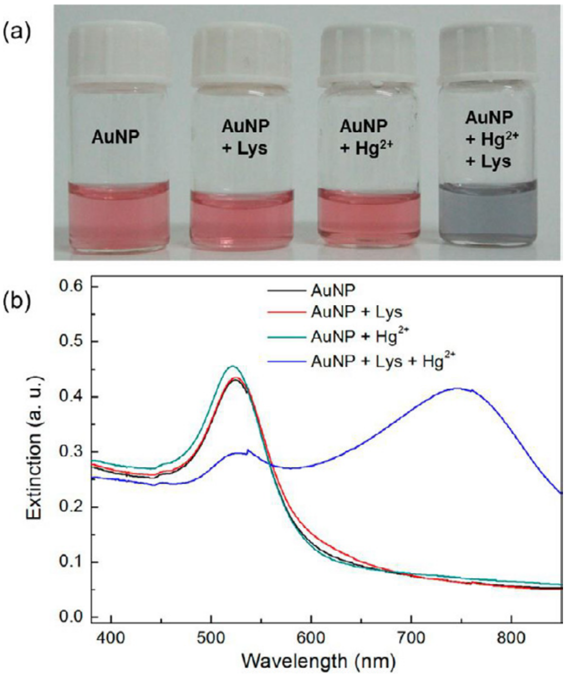

Fig. 2. Colorimetric response of the assay. (a) Photographs of AuNP solutions showing that the color change occurs only in the presence of lysine (0.4 mM) and Hg^{2+} (10 μM). (b) Extinction spectra of the AuNP solutions. Reprinted with permission from ref. 56, Copy right 2014 American Chemical Society.

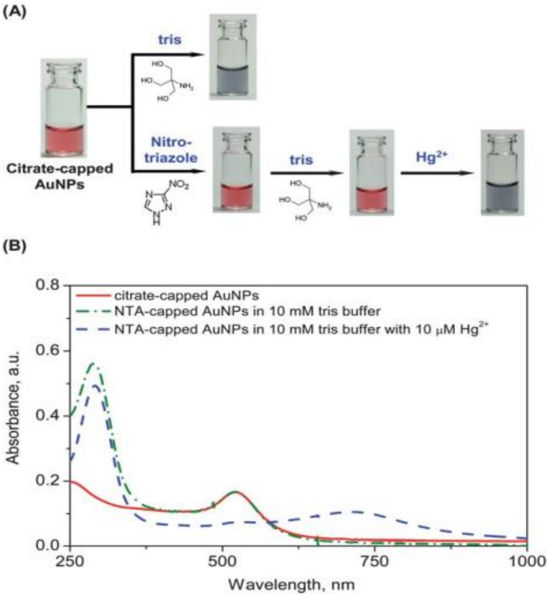

Fig. 3. (A) Color changes of the citrate capped AuNPs upon the addition of 10 mM Tris buffer, 300 mM NTA, and 10 mM Hg^{2+}, respectively. (B) UV-vis absorption spectra of the citrate-capped AuNPs, NTA-AuNP probes in 10mMtris buffer, and NTA-AuNP probes in 10mMtris buffer with 10 mMHg^{2+}, respectively. Reprinted with permission from ref. 63. Copy right 2014 Royal Society of Chemistry 2011.

and AuNPs, it forms Au-S strong covalent bond, and the $-NH_2$ group of 4-ATP remains free. After the addition of Hg^{2+} ion results, the aggregation of 4-ATP capped AuNPs and the color change from ruby red to purple-blue. 3-Nitro-1H-1,2,4-triazole (NTA) functionalized gold nanoparticles are used in the detection of mercury ions (**Fig. 3**) with sensitivity levels as low as 7 nM. NTA capped AuNPs

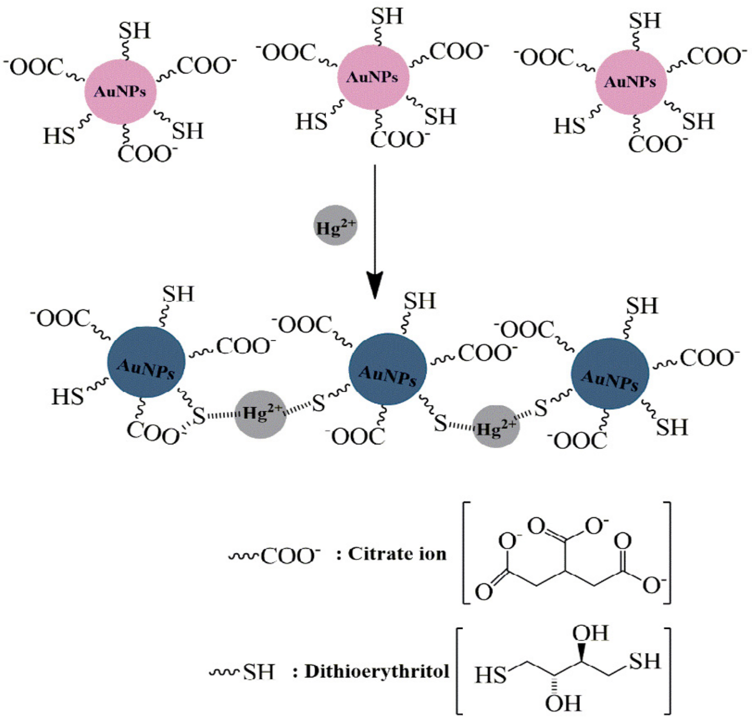

Fig. 4. Proposed mechanism of Mercury (II) sensing.

are achieved due to the strong affinity of nitrogen atoms in the triazole ring for the gold nanoparticle surface. Coordination chemistry between the NTA moieties and Hg^{2+} ions enabled the development of NTA capped AuNPs as a suitable probe for the detection of heavy metal contamination [61].

Dithioerythritol (DTET) modified AuNPs were used in the detection of Hg^{2+} compared to other competing heavy metal ions like Pb^{2+}, Cd^{2+}, and Cu^{2+} due to the strong thiophilic nature of Hg^{2+} and the interaction involved Sulpher-Hg^{2+}-sulphur [62]. Hg^{2+} leads to colorimetric change due to change of SPR absorption and reported the sensing mechanism (**Fig. 4**). The limit of detection was found 100 nM.

AuNPs functionalized with 3-mercapto propionate acid (MPA) and adenosine monophosphate (AMP) was reported by Tseng et al. [63] for colorimetric detection of Hg^{2+}. Owing to the high negative charge density of AMP on each AuNPs surface, MPA/AMP-capped AuNPs are well dispersed in a high-salt solution and the aggregation of MPA-capped AuNPs was induced by sodium ions. The lowest detectable concentration was found 500 nM.

Mercaptopropionic acid-modified AuNPs are highly sensitive for the detection of Hg^{2+} ions in the presence of 2,6-pyridine carboxylic acid (PDCA). This low-cost system has a detection limit of 100 nM and is believed to lay the foundation for the development of nanosensors which could be employed for the detection of Hg^{2+} in both biological and environmental samples [64]. Papain and a 2,6-pyridine dicarboxylic acid (PDCA) functionalized gold nanoparticles (AuNPs) were reported by C. Lai et al [65]. for visual inspection of Hg^{2+} and the detection limit was 9 nM. Papain is a protein with seven cysteine residues and 212 amino acid residues, which can combine with Hg^{2+}, and PDCA is a chelating ligand, which has a strong affinity for Hg^{2+}. 8-hydroxyquinolines (8-HQ) and oxalates modified AuNPs highly selective colorimetric assay for the detection of Hg^{2+}shows quick aggregation of AuNPs leading to the color change from wine red to grey [66]. As Hg^{2+} can bind to quinoline N and carbonyl oxygen atoms and forming a complex with 8-HQ functionalized AuNPs selectively with the help of oxalate, leading to the formation of large aggregation particles. Citrate-capped AuNPs were used for selective determination of Hg^{2+} ion from aqueous solution in the presence of thiourea (TU) [67]. The addition

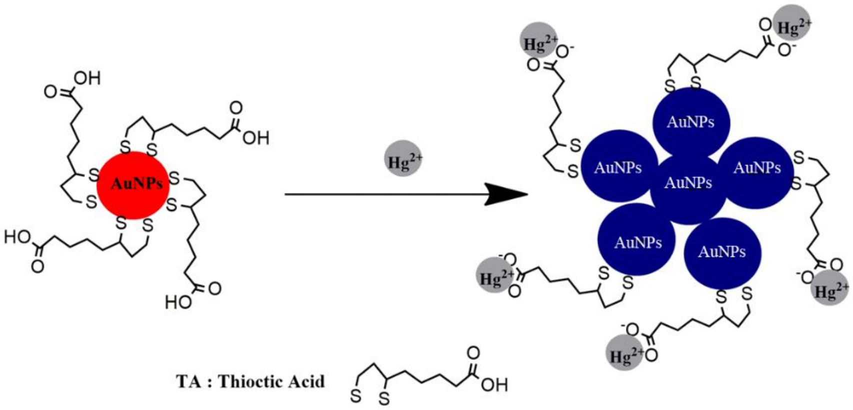

Fig. 5. Proposed mechanism for Hg^{2+} detection using TA@AuNPs colorimetry

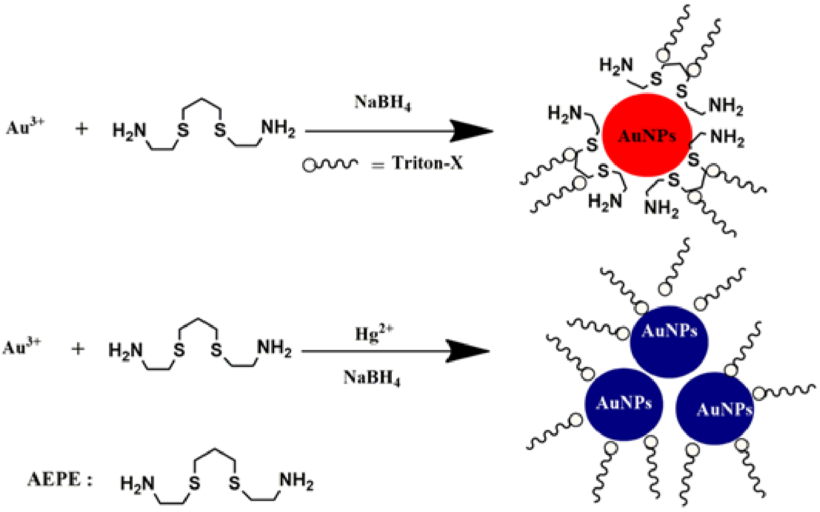

Fig. 6. Proposed mechanism for Hg^{2+} -induced colorimetric response of AEPE capped AuNPs.

of TU into AuNPs resulted in the aggregation of Au NPs with a red-to-blue color change. In the presence of Hg^{2+}, it prevented the aggregation of AuNPs induced by TU, resulting in a reverse color change from blue to purple and finally to wine red. The limit of detection was found to be 100 nM.

The as-prepared Thioctic acid (TA) functionalized AuNPs (TA@AuNPs) were diluted two times by adding an equal quantity of 0.05 M NaCl solution, to produce a color change quickly [68]. The TA-GNPs (**Fig. 5**)) readily formed purple-colored aggregates as they met Hg^{2+} at high ionic strength. The addition of enough salt would screen the repulsion between the negatively charged AuNPs, and lead to the aggregation of the AuNPs followed by a corresponding color change.

The dithia-diaza ligand 2-[3-(2-amino-ethylsulfanyl)-propylsulfanyl]-ethylamine (AEPE) was used as a stabilizer to protect AuNPs from aggregation and to impart highly selective recognition of Hg^{2+} ion over other metal ions **(Fig. 6).** Sodium borohydride reduces the solution of Au(III) ion is in the presence of AEPE and the detergent Triton X-100. This results in the formation of AEPE capped AuNPs and red coloration of the solution. On the other hand, in the presence of Hg(II), the solution turns blue within a few seconds after the addition of borohydride. This can be detected spectrophotometrically or even visually. The method was successfully applied to quantify

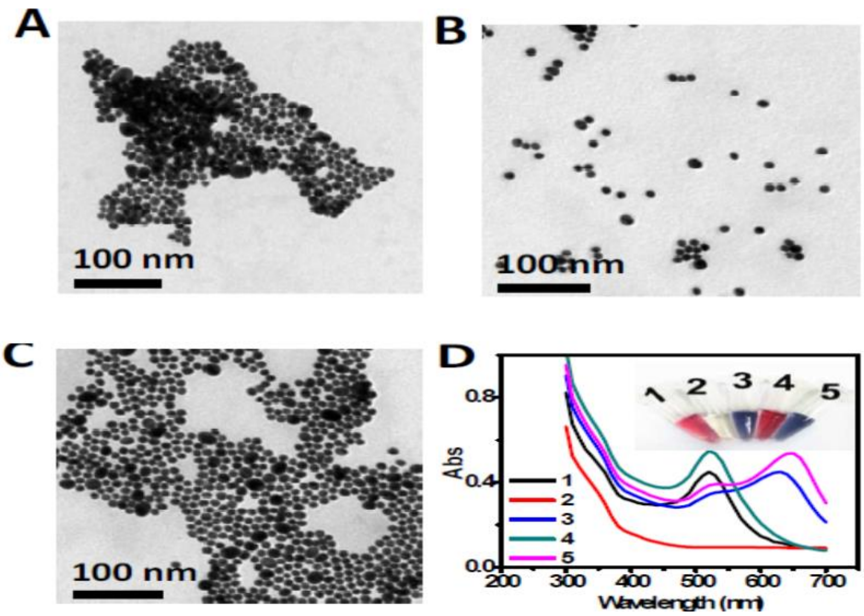

Fig. 7. TEM of different systems: (A) AuNP/CDs composite; (B) AuNP/CDs composite in presence of GSH; (C) AuNP/CDs composite in presence of GSH and Hg^{2+}; (D) UV-Vis spectra of the corresponding of different systems: 1-AuNP, 2-CDs, 3-A, 4-B, 5-C. Inset image is colorimetric response. Reprinted with permission from ref. 75. Copy right 2012 Royal Society of Chemistry.

Hg^{2+} levels in a water sample, with a minimum detectable concentration as low as 35 nM [69].

Jing Fu Liu et al. [70] developed a method based on etching and amalgamation of gold nanoparticles (AuNPs) to detect Hg^{2+} by colorimetric headspace nanosensors. First Hg^{2+} was reduced to Hg (0) by using stannous chloride ($SnCl_2$). Then Hg (0) was headspace extracted into thioglycolic acid (TGA) functionalized gold nanoparticles (AuNPs) in presence of methanol as an extractant. Hg (0) is easily extracted in methanol and reacted with TGA-AuNPs through amalgamation followed by etching TGA on the surface of AuNPs resulting in aggregation of AuNPs and affecting optical properties. Scheme-b shows the mechanism of TGA-AuNPs for the detection of Hg^{2+}. This method can detect Hg^{2+} visually at a level of 10 nM of an environmental water sample. The volatilization and amalgamation processes can be described as follows.

$$Hg^{2+}\,(aq.) + Sn^{2+}\,(aq.) \rightarrow Hg^{0}\,(l) + Sn^{4+}\,(aq.) \qquad (1)$$

$$Hg^{0}\,(l) + 3Au(s) \rightarrow Au_3Hg\,(l)\ \text{(Low Hg atomic content)} \qquad (2)$$

$$2Hg^{0}\,(l) + Au(s) \rightarrow AuHg_2\,(l)\ \text{(High Hg atomic content)} \qquad (3)$$

Quantum dots

Colorimetric detection of Hg^{2+} ions using quantum dot is a very new strategy nowadays as almost all carbon quantum dots [CDs]are showing the fluorescence sensing of analytes. Very few reports have been incorporated in this review. CDs are used for colorimetric detection of Hg^{2+} as CDs are suitable for chemical modification and surface passivation using various organic, inorganic, polymeric as well as biological materials. As a result, the functionalized CDs will interact with metallic nanoparticles (e.g. AuNPs, AgNPs). Hg^{2+}ions can be detected by the aggregation of gold nanoparticles (AuNPs) induced by carbon quantum dots (CDs) with the help of Glutathione (GSH) (Fig. 7). The AuNP/CDs composite forms through the Au-N bond. After adding GSH, it competes with CDs to bind onto the surface of AuNPs and protect to form an aggregation of AuNPs due to strong binding affinity with -SH group of GSH with Au. In presence of Hg^{2+}, GSH can strongly chelate with Hg^{2+} ions and it may facilitate CDs to form an aggregation of AuNPs. Hence for sensitive and selective detection, a colorimetric sensor is established, which can detect up to a limit of 7.5 nM [71]. Carbon nanodots reported by Y. Liang et al. [72] for colorimetric sensing of Hg^{2+} ion with detection limit 5.5×10^{-10} mol L^{-1}. AuNPs are surrounded by a layer of HgS quantum dots to form AuNPs@HgS core-shell structure. The SPR absorption of the gold core was changed due to a

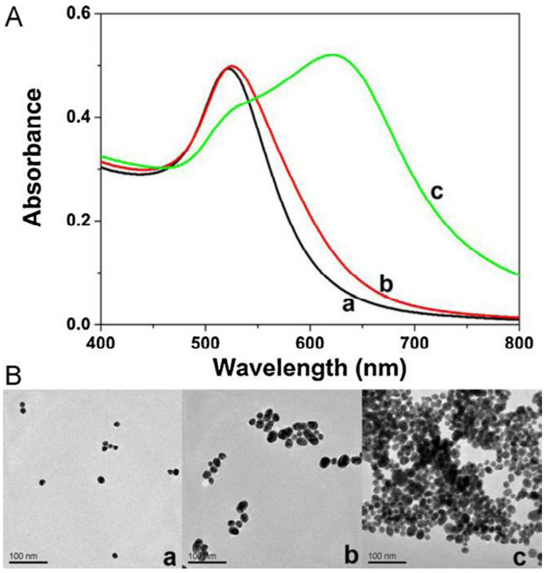

Fig. 8. (A) UV–vis absorption spectra of the citrate-AuNPs (13 nm) (a), P-AuNPs (13 nm) (b) and P-AuNPs (13 nm) in the presence of 20 µM of Hg^{2+} (c). (B) TEM images of the citrate-AuNPs (13 nm) (a), P-AuNPs (13 nm) (b) and P-AuNPs (13 nm) in the presence of 20 µM of Hg^{2+} (c). Reprinted with permission from ref. 76. Copy right 2011 Elsevier.

shell layer of HgS formed on the surface of the Au NPs, which brings the color change from wine red to purple-blue. Therefore, Hg^{2+} can be recognized by visualizing the color change (wine red to purple-blue) with the help of AuNPs@HgS nanostructure, and LOD was found 0.486 nM [73].

Polymers

Papain, a single polypeptide chain containing 212 residues with seven cysteine residues, could selectively bind with Hg^{2+} ion. For colorimetric detection of Hg^{2+} ion, papain functionalized AuNPs can be used for detection of Hg^{2+} in an aqueous solution based on aggregation-induced method indicating a color change from red to blue considering colorimetric detection concentration of ca. 4 mM by lowering the distance of AuNPs, resulting in a shift in the plasmonic band energy to a longer wavelength as well as a color change from red to the blue [74] **(Fig. 8)**.

Guan et al.[75] developed a PGA functionalized gold nanoparticle system (PGA@AuNPs) for the colorimetric detection of Hg^{2+}, where self-assembled of negatively charged PGA begins on the surface of positively charged CTAB-capped AuNPs. Here, Hg^{2+} plays a role in cross-linking agent between the pairs of the PGA functionalized Au NPs resulting in the aggregation of AuNPs and indicates a color change from wine red to dark blue. The colorimetric probe is quite sensitive with a linear range of 0.0110 mM and a real-time detection limit as low as 1.9 nM.

Chitosan (heteropolymer) capped gold nanoparticles (CH@AuNPs) are used in the detection of Hg^{2+}. The presence of reactive amino groups in chitosan binds with Hg^{2+} may help in the aggregation of CH@AuNPs. CH@AuNPs showed a blue shift in the localized surface plasmon resonance (LSPR) when Hg^{2+} ions are added. Interestingly, CH@AuNPs showed a blue shift in the plasmon absorption peak while all the other methods of detection showed a redshift on the addition of Hg^{2+}. The limit of detection of this method was found to be 5 pM, which is the lowest value achieved using the colorimetric method for Hg^{2+} detection [72].

AuNPs stabilized by carboxyl ethyl quaternized cellulose (CEQC) was used for sensitive and selective colorimetric assay to detect cysteine (Cys) and Hg^{2+}in aqueous solutions using. This method is based on the thiophilicity of $Hg^{2+}$and AuNPs as well as the unique optical properties of CEQC stabilized AuNPs, as well as CEQC chains, which are good stabilizing agents for AuNPs even in a high-salt concentration. The addition of Cysteine results in the aggregation of CEQC-stabilized AuNPs, indicating a color change from red to purple-blue. Owing to the strong affinity between Hg^{2+} and the S-H group of cysteine (**Fig. 9**) than AuNPs, it can remove the Cys and trigger AuNPs aggregate redispersion again. Thus, a novel off–on

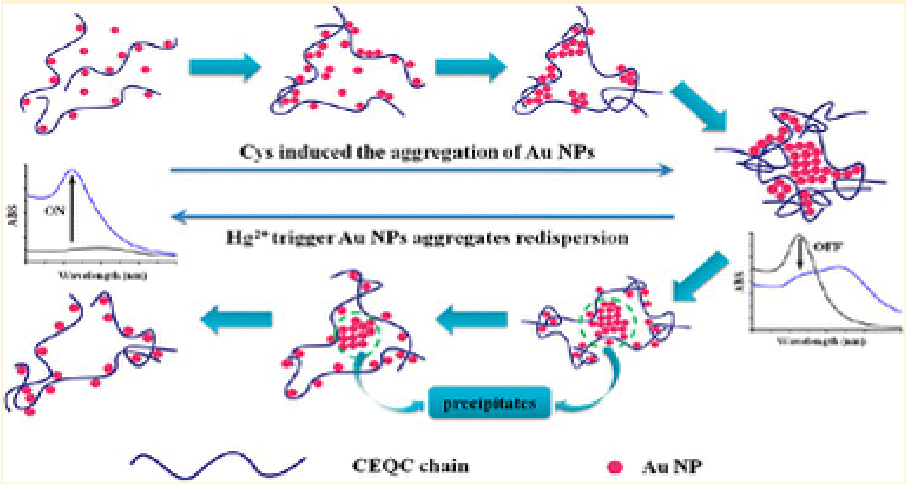

Fig. 9. Carboxylethylquaternizedcellulose stabilized AuNPs for the detection of Hg^{2+}. Reprinted with permission from ref.79. Copy right 2013 American Chemical Society.

colorimetric sensor has been established for Cys and Hg^{2+}detection. This assay was utilized to selectively detect Cys and Hg^{2+}having detection limits of 20 and 40 nM in aqueous solutions, respectively [77].

Surfactants

Tween 20 modified citrate stabilized AuNPs are employed for the detection of Hg^{2+}. Citrate-capped AuNPs modified with Tween 20 are stable at high ionic strength in absence of Hg^{2+}. However, when Hg^{2+} ions were added, the same was reduced by citrate ions, and Hg–Au alloys are formed on the surface of the AuNPs, and as a result, Tween 20 was removed from the NP surface, resulting in AuNPs aggregation to indicate a color change from red to purple. In this way, Hg^{2+} was detected selectively by Tween 20-AuNPs at a level of 0.1 mM with a linear range of 200–800 nM [78].

COLORIMETRIC DETECTION OF HG²⁺ USING FUNCTIONALIZED SILVER NANOPARTICLES (AGNPS)

Researchers utilized Silver nanoparticles (AgNPs) in a wide range for monitoring the environment with high sensitivity, good selectivity, and biocompatibility because of their intensive surface plasmon resonance (SPR) bands [79]. Certain AgNPs-based colorimetric sensors have been successfully applied to probe Hg^{2+} based on the Hg^{2+} induced aggregation of functionalized AgNPs, which results in a color change and UV-Vis spectral response. The year-wise statistics for the colorimetric determination of Hg^{2+} ion are as follows (**Fig. 10**).

Organic & Inorganic ligands functionalized AgNPs for Hg^{2+} detection

A novel p-phenylenediamine (p-PDA) functionalized AgNPs (p-PDA@AgNPs) was used to detect Hg^{2+} in aqueous medium (**Fig. 11**). This system showed a visually detectable color change from brownish-yellow to colorless for the selective detection of highly toxic Hg^{2+} ions. The developed system is simple and sensitive to detect Hg^{2+} with a detection limit was found to be 0.80 µM [80]. The free -NH_2 groups of p-PDA may interact with Hg^{2+} ion through the bridging fashion and results in the aggregation of p-PDA@AgNPs.

The addition of H_2O_2 to the mixture of silver nanoparticles (AgNPs) and Hg^{2+}induced color changes of the solution within several seconds even at 2.0 nM Hg^{2+} (**Fig. 12**). Upon the addition of H_2O_2 to the mixture of Cit-AgNPs with an increasing concentration of Hg^{2+} (from 50 to 1000 nM), the color changed from yellow, salmon pink to rose pink within several seconds. The outstanding sensitivity and selectivity property for Hg^{2+}, resulted from the AgNPs mediated reduction of Hg^{2+} to elementary Hg in the presence of H_2O_2, causing the aggregation and the colorimetric response of AgNPs [81].

N-(2-hydroxy benzyl)-valine (VP) and N-(2-hydroxy benzyl)-isoleucine (ILP) organic ligands have been utilized as reducing and surface functionalizing agents in the synthesis of silver nanoparticles (AgNPs)with metal ion interacting functionality. VP and ILP metal interacting

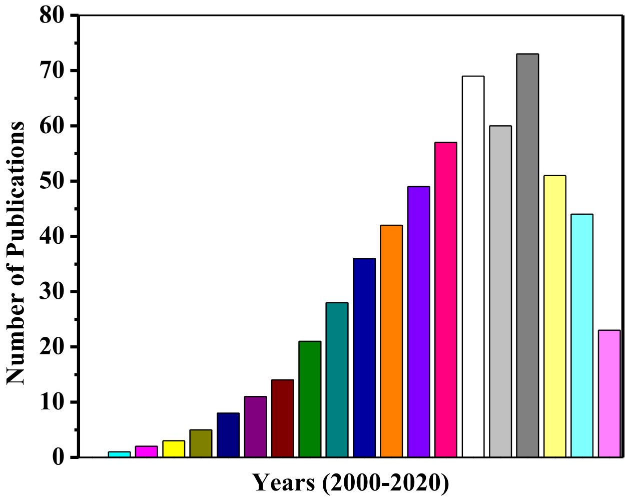

Fig. 10. Year wise statistics for the colorimetric detection of Hg^{2+} ion using functionalized AgNPs (2000-2020, Left to Right).

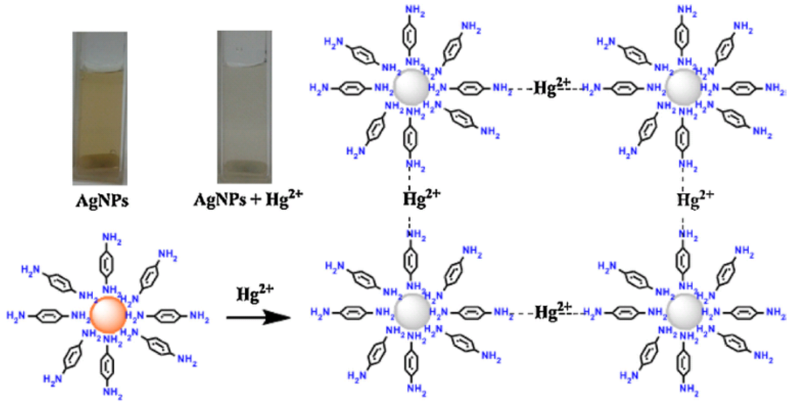

Fig. 11. Scheme for interaction of Hg^{2+} by p-PDA capper AgNPs. Reprinted with permission from ref.82 Copy right 2013 Elsevier.

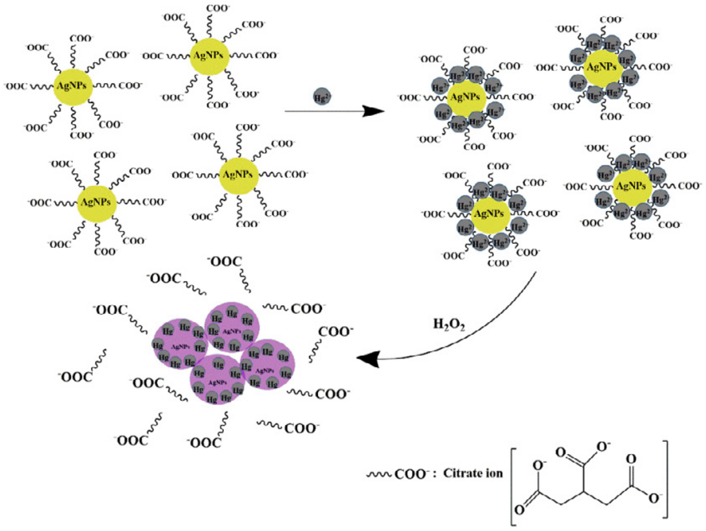

Fig. 12. Proposed mechanism for the Hg^{2+}-induced-colorimetric response of AgNPs in presence of H_2O_2.

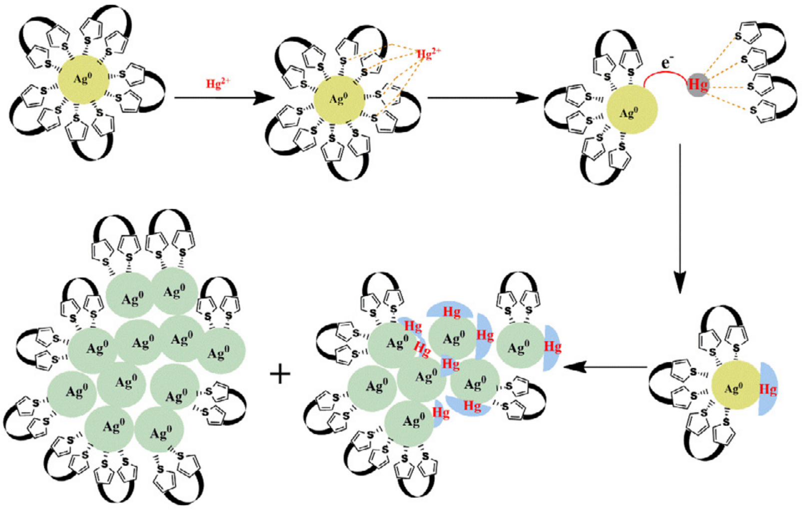

Fig. 13. Proposed mechanistic aspect of Hg^{2+} sensing by ThC-AgNPs.

ligands functionalized AgNPs exhibited selective colorimetric sensing of toxic Hg^{2+} in aqueous solution at ppm-level. The colorimetric sensitivity and metal ion selectivity of VP- and ILP-AgNPs were modulated by incorporating co-stabilizing agents [82]. A. Nayal et al. reported [83] the synthesis of 1,2,3-triazole ring stabilized AgNPs for colorimetric determination of Hg^{2+} from aqueous solution. During the addition of Hg^{2+} on the triazole stabilized AgNPs, the color of the solution change from yellow to colorless due formation of Ag-Hg amalgam and aggregation formed in solution.

Mustafa U. Gurbuz et al.[84] developed a method for colorimetric detection of Hg^{2+} using dendrimer encapsulated AgNPs (AgDENPs). They synthesized it by using Tris (2-aminoethyl) amine (TREN) cored and amine-terminated generation-4 poly (amidoamine) dendrimer (PAMAM), $T4.NH_2$. Here $T4.NH_2$ acts as a stabilizer. In this method, the detection limit of Hg^{2+} was observed at a level of 1.18 ppb (5.88 nM). Moreover, the developed AgDENPs were tested against common cations present in the environment like Co^{2+}, Cu^{2+}, $Pb^{2+,}$ Cd^{2+}, Ni^{2+}, Zn^{2+}, Ba^{2+}, $Ca^{2+,}$ and Al^{3+} and found to be specific for Hg^{2+}. G. Maduraiveeran et al.[85] that NAD (nicotinamide adenine dinucleotide) in aqueous solution functionalize with AgNPs for selective and sensitive detection of Hg^{2+} ions in presence of other common cations found in environmental water. NADH reduces and stabilizes the silver nanoparticle and CTAB (cetyltrimethylammonium bromide) was added to grow AgNPs. The detection limit of Hg^{2+} was found to be 0.02 nM. G. Vyas et al. [86] synthesized Calixarene-caped, namely Thiophene-substituted calixarene derivative (ThC) silver nanoparticle (**Fig. 13**) to detect Hg^{2+} colorimetrically. With the addition of Hg^{2+} containing the sample, calixarene moiety was replaced by Hg^{2+} on the surface of the functionalized nanoparticle to form Ag-Hg amalgam. In this method, functionalized nanoparticles can detect Hg^{2+} at the limit of 0.5 nM.

Natural and biofunctionalized AuNPs for Hg^{2+} detection

The natural algal polysaccharide carrageenan was used for the greener synthesis of silver/silver chloride nanoparticles (Carr–Ag/AgCl NPs) without any toxic chemicals. This robust, highly selective, and sensitive colorimetric sensing of Hg^{2+} ions using Carr–Ag/AgCl NPs without any further surface modification. The dark brown color of a solution of Carr–Ag/AgCl NPs turned to white in a concentration-dependent manner with the addition of Hg^{2+}ions, confirming the interaction of Carr–Ag/AgCl NPs with Hg^{2+} ions. The detection limit was observed as low as 1 µM. This portable and cost-effective method for Hg^{2+} ion sensing is widely applicable in on-field qualitative and quantitative measurements of Hg^{2+} ions (**Fig. 14**) in environmental or biological samples [87]. Biofunctionalized AgNPs can be synthesized by using Hibiscus Sabdariffa (Gongura) plant extracts leaves (HL) and stem (HS)) and this will

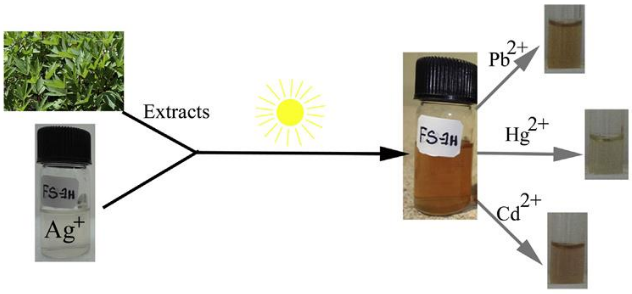

Fig. 14. Bio-functionality of green synthesized AgNPs from Hibiscus Sabdariffa plant extracts were successfully utilized for selective colorimetric sensing of potentially health and environmentally toxic metal ions such as Hg^{2+}, Cd^{2+} and Pb^{2+} in aqueous solution. Reprinted with permission from ref.89. Copy right 2017 Elsevier.

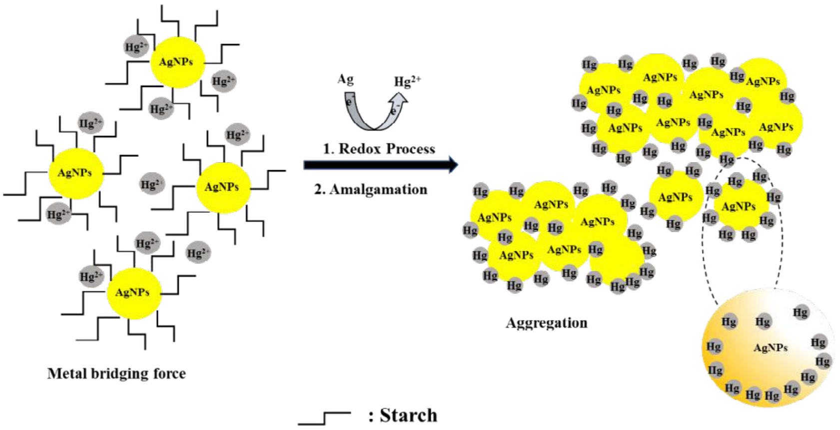

Fig. 15. The proposed mechanism for the interaction between starches coated AgNPs and Hg^{2+} solution.

be successfully utilized for selective colorimetric sensing of potential health and environmentally hazardous Hg^{2+} at ppm level in aqueous solution, where a distinguishable color for the metal ion was observed. The influence of extract preparation condition and pH were also explored on the formation of AgNPs. Differences in selectivity and sensitivity were observed for different parts of the plant while AgNPs were synthesized. The direct correlation between the stability of green synthesized AgNPs and their antibacterial effects has been established at different pH. The selective colorimetric sensing of toxic metal ions and the antimicrobial effect of green synthesized AgNPs demonstrated the multifunctional applications of green nanotechnology [88].

A sensitive and selective Hg^{2+} optical sensor has been developed based on the redox interaction of Hg^{2+} (**Fig. 15**) with starch-coated silver nanoparticles (AgNPs) [89] in the presence of 0.005 mol L^{-1} HNO_3. Experiments performed demonstrated that metal ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+}, Co^{2+}, and Ni^{2+}) do not interfere under the same conditions, as the absence of oxidative activity of these ions, which drives the high selectivity of the proposed optical sensor towards Hg^{2+}.

Green synthesized dextrose and maltose-reduced silver nanoparticles (AgNPs) were investigated for colorimetric sensing of metal ions at different concentrations and reaction times. Both maltose and dextrose-reduced AgNPs were found to be highly sensitive and selective to Hg^{2+}. This was accompanied by a color change from yellowish solution to colorless for the presence of Hg^{2+}ions. This also showed that dextrose-reduced Ag-NPs resulted in better colorimetric sensing of metal ions than maltose-reduced Ag-NPs. Both Ag-NPs solutions were highly sensitive and selective towards Hg^{2+} ions at a lower concentration up to 1 pM [90].

An Ag NPs-based Hg^{2+} sensor was designed

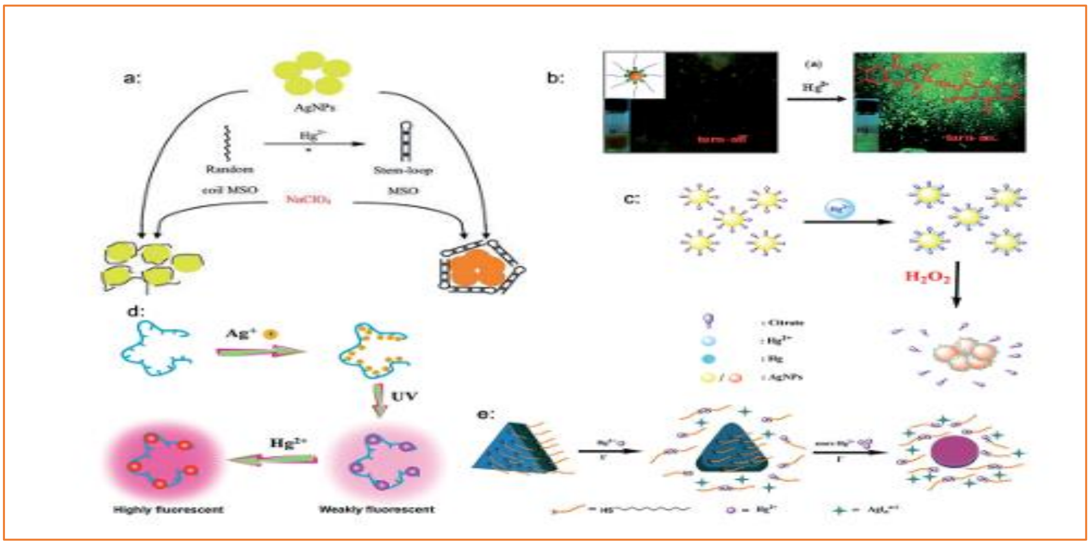

Fig. 16. Schematic strategies for the colorimetric sensing mechanism of AgNPs-based sensor for Hg^{2+}. Reprinted with permission from ref.93. Copy right 2011 Royal Society of Chemistry.

Table 2. List of ligands functionalized AuNPs and AgNPs with respect to their various parameters

Analytical Parameters	Functionalized Ligands	Linear Range	Limit of Detection nM)	Applications	Ref.
AuNPs	Lysine	1 nM to 1 µM	2.9	Hg^{2+}	54
AuNPs	4-ATP	-	0.0005 µg/mL	Hg^{2+}	60
AuNPs	NTA	10 to 500 nM.	50	Hg^{2+}	61
AuNPs	DTET	-	100	Hg^{2+}	62
AuNPs	MPA/AMP	1 -100 µM	500	Hg^{2+}	63
AuNPs	MPA/PDCA	250–500 nM	100	Hg^{2+}	64
AuNPs	Papain & PDCA	0.01 to 14 mM	9	Hg^{2+}	65
AuNPs	8-HQ & Oxalate	100 µM to 10 nM	10	Hg^{2+}	66
AuNPs	TU	100 to 1000 nM	40	Hg^{2+}	67
AuNPs	TA	10 nM -20µM	10	Hg^{2+}	68
AuNPs	AEPE	1–9.0 µM	35	Hg^{2+}	69
AuNPs	PGA	0.01-10 µM	1.9	Hg^{2+}	70
AuNPs	Chitosan	-	5 pM	Hg^{2+}	71
AuNPs	CEQC	1-10 µM 3–24 µM	20 & 40	Cys & Hg^{2+}	72
AuNPs	Twen-20	-	0.01 µM	Ag^{+} & Hg^{2+}	73
AuNPs	Papain	-	200	Hg^{2-}, Pb^{2-} & Cu^{2+}	74
AuNPs	MUA & Amino acids	1–50 µM	-	Hg^{2-}, Pb^{2-} & Cd^{2+}	55
AuNPs	DNA	1-100 nM	10 nM	Hg^{2+}	69
AgNPs	p-PDA	-	0.80 µM & 1.29 µM	pH, Hg^{2+} & Fe^{3+}	80
AgNPs	VP & ILP	-	-	Cd^{2+}, Hg^{2-} & Pb^{2+}	82
AgNPs	Steroidal 1,2,3-triazole	-	100 µM & 200 µM	Hg^{2-} & I^{-}	83
AgNPs	dendrimer		5.88	Hg^{2+}	84
AgNPs	NAD		0.02	Hg^{2+}	85
AgNPs	ThC		0.5	Hg^{2+}	86
AgNPs	Starch	25 to 500 μgL^{-1}	0.9 μgL^{-1}	Hg^{2+}	89
AgNPs	Graphene oxide	5-75 µM	0.59 µM	Hg^{2+}	92

by Roy e al. [91] using riboflavin (R) which acted as a reducing and stabilizing agent through a “turn off”–“turn on” mechanism in an aqueous medium **(Fig. 16).** Riboflavin keeps itself in ‘turn off’ condition when it is bound with the Ag NPs. After adding Hg^{2+}, the strong T–Hg^{2+}–T bonds are formed and it freed the Ag NPs as a result the system is converted to a ‘turn on’ condition with a sudden color change from deep orange to bright yellow. The sensing time was found to be 1.0 min and the detection limit was a lower value of 5 nM. Functionalization of ligands using AuNPs and AgNPs concerning various parameters are summarized in Table 2.

ABBREVIATION TABLE

ICP-MS	Inductively Coupled Plasma Mass Spectrometry,
ASS	Atomic Absorption Spectrometry
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
HPLC	High Performance Liquid Chromatography
SPR	Surface Plasmon Resonance
NPs	Nanoparticles
AuNPs	Gold Nanoparticles
AgNPs	Silver Nanoparticles
TOAB	Tetraethylammonium Bromide
CTAB	Cetyltrimethylammonium Bromide
NHC	N-heterocyclic carbene
$NaBH_4$	Sodium Borohydride
DMF	N, N-dimethylformamide
TX-100	Triton X-100
MUA	11-Mercaptoundecanoic Acid
Lys	Lysine
DTET	Dithiothreitol
4-ATP	4-Amino Thiophenol
NTA	3-Nitro-1H-1,2,4-Triazole
MPA	3-Mercaptopropionate Acid
AMP	Adenosine Monophosphate
PDCA	2,6-Pyridine Carboxylic Acid
8-HQ	8-Hydroxyquinolines
TU	Thiourea
TA	Thioctic Acid
AEPE	2-[3-(2-amino-ethylsulfanyl)-propylsulfanyl]-ethylamine
TGA	Thioglycolic Acid
CDs	Carbon Quantum Dots
GSH	Glutathione
LSPR	Localized Surface Plasmon Resonance
CEQC	Carboxyl Ethyl Quaternized Cellulose
Cys	Cysteine
p-PDA	p-phenylenediamine
VP	N-(2-hydroxybenzyl)-Valine
ILP	N-(2-hydroxybenzyl)-Isoleucine
NAD	Nicotinamide Adenine Dinucleotide

CONCLUSIONS AND FUTURE PROSPECTS

In conclusion, the colorimetric detection of Hg^{2+} has attracted much more attention to qualitative and quantitative information simply by visual inspection without using expensive instrumentation and laboratory setup. In this review, we have attempted to provide the research progress on AuNPs and AgNPs functionalized with various types of ligands such as organic ligands, amino acids, polymers, DNA, peptides, surfactant, and quantum dots, etc. materials for selective colorimetric detection of Hg^{2+} ion. The accurate synthesis and functionalization of AuNPs and AgNPs are challenging for applying to the environment due to their critical colloidal stability. The interaction with the protein, cell, complex biological molecules as well as various metal ions (analytes) depends on the proper selection of ligands with their hydrophobic/hydrophilic nature which is directly related to the reactivity.

There is still enough work that has been done regarding selectivity, sensitivity, reliability, and repeatability in terms of sensors. But still, there is enough future scope for selective detection of metal ions using proper functionalization of AuNPs and AgNPs.

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CONFLICTS OF INTEREST

The authors declare that there are no conflicts of interest.

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