Advances for the colorimetric detection of Hg$^{2+}$ in aqueous solution†

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Exposure to mercury ions, even at very low levels, is known to cause a wide variety of diseases in the brain, kidney, and central nervous system, which is an increasing serious problem for human beings and the environment. Accordingly, great efforts have been devoted to the development of colorimetric sensors, which can selectively and conveniently detect Hg$^{2+}$. In this feature article, to present the readers a better understanding of the specific methods and their mechanisms, we will highlight colorimetric sensors according to their receptors into several categories, including organic dye-based sensors, complex based sensors, polymer based sensors, and nanoparticles based sensors, which are mentioned in the literature and our own work during the recent years.

1. Introduction

With the rapid development of modern industries and modern agriculture, the situation of environmental contamination by heavy metals is getting increasingly serious. Heavy metals are routinely released from coal-burning power plants, volcanic emissions, mining, and solid-waste incineration. Among all the heavy metals, Hg$^{2+}$ is one of the most toxic and dangerous because of its strong affinity to S-containing ligands and results in the blocking of sulphydryl (–SH) groups in proteins and enzymes. Further, Hg$^{2+}$ is not biodegradable and accumulates in animal and human bodies, which causes the dysfunction of cells and results in a wide variety of diseases related to brain, kidney, and central nervous system.1,2 Thus, a convenient, rapid, highly sensitive and on-site detection of Hg$^{2+}$ is highly desirable.

There are several classical mercury detection methods, including atomic spectrometry,3,4 inductively coupled plasma mass spectrometry,5 reversed-phase high-performance liquid chromatography,6 electrochemistry7 and fluorescent spectrophotometry.8 Their excellent performance, however, are achieved at the expense of complicated and expensive instrumentation and cumbersome laboratory procedures, which cannot be straightforwardly and conveniently used.9,10 There is a growing need for rapid on-site analysis with chemosensors that are capable of detecting toxic metal ions on a real-time basis. In this regard, colorimetric detection has attracted particular attention for offering qualitative and quantitative information with naked-eye discernibility without the use of expensive equipment.11–13

In general, the colorimetric chemosensors of Hg$^{2+}$ can be prepared through the right combination of receptors and chromophores.2,11–15 To give readers a systematic overview, the following sections will highlight the recent developments, applications and mechanisms of colorimetric sensors for Hg$^{2+}$ according to their receptors, i.e., organic molecule, complex, polymer and nanoparticle-based colorimetric sensors would be introduced and sequentially discussed.

2. Organic dye-based sensors

2.1 Polyether-based sensors

Organic dye-based sensors have attracted extensive attention because of their advantages of solution processability, facile and scalable synthesis, and tunable chemical and physical properties via the molecular design. Various kinds of organic materials with different structures and tunable optical properties have been successfully used as colorimetric chemosensors.16–19 Among all the identified organic sensors, polyether compounds with more than one ether group, i.e., oxygen atoms, nitrogen atoms or sulfur atoms as multidentate ligands, can strongly and selectively coordinate to different heavy metal ions. For example, Sancenón et al.20 reported that a qualitative analytic receptor containing pendant aza-oxa binding sites could selectively coordinate to Hg$^{2+}$ with a corresponding color change from yellow-orange to red at a molar ratio of ligand : metal as 1 : 1.

Li and co-workers21 developed a water-soluble Hg$^{2+}$ chemosensor using hemicyanine as the colorimetric reporting group and a NO$_2$Se$_2$ chelating unit as the ion binding site. The chemosensor not only possessed good selectivity to Hg$^{2+}$ over other
chemically similar ions, it was also discernible to the naked-eye with a colorimetric change from red to colorless. The detection limit was estimated to be \(5.0 \times 10^{-8}\) M, meeting the discharge limit for industrial waste water according to the China SA standard. The sensing mechanism was attributed to the intramolecular charge transfer (ICT), through which the metal ionophore was incorporated into the electron donor moiety of the chromophore.

Kadarkaraisamy and co-workers\(^{22}\) reported a terthiophene-based colorimetric sensor, combining linear \(\pi\)-conjugated aromatic compounds and annular macrocycles. Upon \(\text{Hg}^{2+}\) addition, the sensor qualitatively showed an intense color change from light-yellow to red. This was attributed to the interaction between \(\text{Hg}^{2+}\) with the sulfur atoms of the terthiophene unit, which lead to the formation of a charge transfer band due to the partial oxidation of the terthiophene unit. This simple mercury ion sensing mechanism considerably differs from other numerous photoinduced electron transfer (PET) sensors, which couple a selective receptor to the fluorophore.\(^{21}\)

Xie and co-workers\(^{23}\) synthesized an efficient and visible light excitable \(\text{Hg}^{2+}\) sensor by joining 4-amino-7-nitro-benzoxadiazole fluorophore to a thiaazacrown ether via an ethylene spacer. When the binding ratio with \(\text{Hg}^{2+}\) was 1 : 1, the absorption peak of the sensor red shifted from 466 to 513 nm, which manifested as a color change from pale yellow to magenta. The limit of detection for \(\text{Hg}^{2+}\) was estimated to be \(2.2 \times 10^{-7}\) M with a linear range from 0.4 \(\mu\)M to 8 \(\mu\)M. Moreover, the removal of the ethylene spacer would considerably reduce the \(\text{Hg}^{2+}\) binding capability of the compound, while it increased its fluorescent quantum yield. This work shows that the spacer group between the signaling moiety and the binding site can have significant influence on the optical property and colorimetric performance of the chemosensor.

Tian and co-workers\(^{24}\) reported an ortho-thiaazacrown ether substituted \(N\)-aryl-9-aminobenzo[\(b\)]quinolizinium \(\text{Hg}^{2+}\) sensor (Fig. 1a). The 1 : 1 stoichiometry of the sensor–\(\text{Hg}^{2+}\) complex in buffer–methanol (1 : 3) had been studied in detail. Notably, the change in the optical absorption of the sensor on the addition of \(\text{Hg}^{2+}\) could be recognized by the naked eye as the colour changed from yellow to red. The limit of detection is 0.10 \(\mu\)M, with a linear range from 0 to 75 \(\mu\)M. It is worth noting that benzo[\(b\)]quinolizinium derivatives represent one of the few types of chemosensors that allows discrimination between \(\text{Hg}^{2+}\) and competing thiophilic cations, such as \(\text{Ag}^+\) or \(\text{Pb}^{2+}\) ions, which often interfere with \(\text{Hg}^{2+}\) detection.

Zhang and co-workers\(^{25}\) showed that 4-(bis(2-(ethylthio)ethyl)amino)-\(N\)-n-butyl-1,8-naphthalimide formed a 1 : 1 complex with \(\text{Hg}^{2+}\). Because of the combined contributions of the PET and the ICT processes, the solution showed a colour change from bright yellow to colorless in the presence of \(\text{Hg}^{2+}\).

A multifunctional dye, 4,4’-bis-(carboxyl phenylazo)-dibenzo-18-crown-6 dye, with a crown ether ring, azo and carboxyl groups was designed by our group.\(^{13}\) The dye exhibited a well-defined \(\text{Hg}^{2+}\)-selective ratiometric colorimetric sensing behavior. The recognition for \(\text{Hg}^{2+}\) had a linear range of 2.5–58 \(\times 10^{-7}\) M with a 0.9978 correlation coefficient. The method was applied for the analysis of 3 environmental water samples with a detection limit of 2.9 \(\times 10^{-8}\) M and a relative standard deviation lower than 3.7% (\(n = 5\)). The good \(\text{Hg}^{2+}\) selectivity was achieved by tailoring the size of the crown-ether ring for optimal \(\text{Hg}^{2+}\) binding and by using \(-N=\text{N}-\) groups as the binding sites for other coexisting ions to reduce their interferences (Fig. 1b). The \(-\text{COOH}\) groups were introduced to increase the aqueous solubility of the sensor.

Recently, using 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid, tri-\(\text{tert}\)-butyl ester, as the binding site and the cyclen-nitrobenzoxadiazole (NBD), chromophore, as the reporting chromogenic subunit, Choi and co-workers\(^{26}\) developed a novel \(\text{Hg}^{2+}\)-selective colorimetric sensor. as shown in Fig. 1c. Because of the strong interaction of \(\text{Hg}^{2+}\) with the lone pair of NBD nitrogen atom, which increases the energy of the charge transfer from the amine fragment to the nitro group, the color of the sensing system changed from pink to yellow in the presence of \(\text{Hg}^{2+}\). The ratiometric plot of \(A_{508}/A_{508}\) as a function of the \(\text{Hg}^{2+}\) concentration shows an almost linear trend up to \(5.0 \times 10^{-4}\) M of \(\text{Hg}^{2+}\), with a detection limit of \(1.5 \times 10^{-6}\) M (0.3 ppm) in aqueous environments.

### 2.2 Squaraine-based sensors

Squaraine is one of the most popular classes of colorimetric molecular sensors. Its rigid \(D-\pi-A-\pi-D\) conjugation endows the molecule with a strong absorption from red to the near-IR region.\(^{27,28}\) In particular, its detection sensitivity in the near-IR region can be significantly improved by excluding the background absorption in the visible region. With this merit, many squaraine derivatives have been designed and applied for detecting heavy metal ions. For example, Avirah and co-workers\(^{29}\) demonstrated the application of a semi-squaraine dye (SSQ) (Fig. 2a) as a novel probe for the qualitative detection of \(\text{Hg}^{2+}\). The addition of \(\text{Hg}^{2+}\) to the solution of the SSQ resulted in the complete disappearance of the absorbance at 472 nm, with a visual color change from deep yellow to colorless. The high selectivity for \(\text{Hg}^{2+}\) is attributed to the soft acid nature and the size effect of the mercury ion. The interfacing oxygen atoms

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Fig. 1 The proposed schematic diagrams of the complexes formed between \(\text{Hg}^{2+}\) and polyether-based sensors.
of the carbonyl groups in the SSQ can exclusively coordinate with Hg$^{2+}$ and result in an obvious color change.

To improve the selectivity and sensitivity for Hg$^{2+}$ detection, we had designed a sensor by attaching a signaling squaraine moiety to two crown-ether rings custom-sized for catching the Hg$^{2+}$ ion (Fig. 2b). Upon the addition of Hg$^{2+}$, the color of the sensor solution changed from blue to colorless. Under the optimum conditions, the detection had a linear range of 7.5–150 × 10$^{-8}$ M with a correlation coefficient of 0.9983 with a limit of detection of 5.6 × 10$^{-9}$ M. The relative standard deviation was lower than 2.4%.

Further, Wang and co-workers$^{31}$ developed a dithiosquarylium (DTSQ)-based Hg$^{2+}$-selective qualitative chemosensor, which could exclusively react with Hg$^{2+}$ with an irreversible colour change because of the Hg$^{2+}$-triggered desulfurization of dithiosquarylium into its oxygen analogue squarylium dye (SQ), as shown in Fig. 2c. The action mechanism was attributed to the sulfur atoms in DTSQ that coordinated with Hg$^{2+}$ at a ratio of DTSQ : Hg$^{2+}$ = 1 : 2 and resulted in immediate visual spectral changes. This transformation is unique and specific for Hg$^{2+}$.

Taking advantage of the specific aggregation effect of squaraine molecules, Chen and co-workers$^{32}$ designed a squaraine-based colorimetric sensor using (phenylazanediyl)-bis-(ethane-2,1-diy)-bis-diethyl-carbamodithioate as the binding groups. Upon the addition of Hg$^{2+}$, the colour of the solution dramatically changed from purple to blue. The detection limit reached 7.1 × 10$^{-9}$ M with a linear concentration range from 0.13 to 0.63 μM. The colour change was attributed to the formation of the 1 : 2 binding mode of squaraine to Hg$^{2+}$ and the steric hindrance of the coordinated Hg$^{2+}$ complex with the side arms, which induced the deaggregation of the H-aggregates, as shown in Fig. 2d.

Recently, Shafeekh and co-workers$^{33}$ reported an unsymmetrical squaraine as a colorimetric probe for the detection of Hg$^{2+}$ in methanol. Upon the addition of Hg$^{2+}$, the colour of the solution changed from blue to violet, making possible the detection of the presence of mercury with the naked eye with the lowest detection concentration of Hg$^{2+}$ ca. 18.0 × 10$^{-6}$ M. The unsymmetrical squaraine formed a unique 1 : 1 adduct with Hg$^{2+}$ through the phenyl squarate carbon–carbon bond, as shown in Fig. 2e. Importantly, the substitution of a sulfur-alkyl group enhanced the binding affinity towards Hg$^{2+}$ in methanol and facilitated the resultant addition reaction.

### 2.3 Rhodamine-based sensors

Rhodamine and its derivatives are another common type of organic chemodosimetric sensors for various heavy metal ions because of their special photophysical properties.$^{34,35}$ Rhodamine derivatives are non-fluorescent and colourless, whereas the ring-opening of the spirolactam moiety produces a strong fluorescent centre, which provides a clear signal for a colorimetric detection. Yang and co-workers$^{36}$ developed a rhodamine 6G derivative with a spirocyclic form for detecting Hg$^{2+}$ in aqueous solutions. The addition of Hg$^{2+}$ to the solution of the dye caused instantaneous ring-opening (Fig. 3) accompanied with a change in the colour of the solution to pink with a strong yellow fluorescence. The system, which utilized an irreversible Hg$^{2+}$-promoted oxadiazole forming reaction of the rhodamine derivative, was monitored by colorimetric and fluorescent intensity changes that instantaneously responded at room temperature in a 1 : 1 stoichiometric manner to the amount of Hg$^{2+}$ with excellent sensitivity below 2 ppb. The findings suggest that this method could serve as the foundation of practical chemodosimeters for rapidly determining Hg$^{2+}$ concentrations in aqueous environments.

Kim and co-workers$^{37}$ investigated rhodamine B derivatives bearing mono and bis-boronic acid groups as the binding sites, for the first example of a reversible fluorescent chemosensor for Hg$^{2+}$. The addition of Hg$^{2+}$ induced a selective color change from colorless to dark pink with a detection limit of 30 μM. These changes were due to the opening of the spirolactam ring (nonfluorescent) to form a strongly fluorescent amide. Their study successfully demonstrates that the boronic acid group can serve as a unique and novel ligand for metal ion recognition.

Ahamed and co-workers$^{38}$ also established a reversible sensor for Hg$^{2+}$ with an “Off-On-Off” functionality with a pyrene and rhodamine 6G functionalized chemosensor. The selective OFF–ON sensing of Hg$^{2+}$ was similar to the report by

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**Fig. 2** The proposed binding models of solvated Hg$^{2+}$ with the reported squaraine dyes.

**Fig. 3** Hg$^{2+}$-induced ring opening and the cyclization of rhodamine 6G.
Kim, and the on–off nature was confirmed by the addition of EDTA to the resultant solution containing Hg²⁺ in dry CH₂CN. Other rhodamine-based colorimetric chemosensor bearing nitrobenzo-xadiazole, thiol and carboxylic acid groups, thiocarbonyl and benzothiazole groups, thio ether, and benzothiazole moiety had been designed and developed for sensing Hg²⁺ based on its ability to open the spirolactam ring of the rhodamine moiety and the formation of 1 : 1 sensor–Hg²⁺ complexes.

2.4 Other organic molecular sensors

This section summarizes other organic colorimetric chemosensors for Hg²⁺, which are not based on the polyether, squaraine or rhodamine moieties. Representative, Cheng and co-workers reported two colorimetric chemosensors (S1 and S2) for Hg²⁺ (Fig. 4a), in which the azobenzene moiety acted as the electron donor and the aldehyde group acted as the electron acceptor. In the presence of just 20 μM Hg²⁺, the sensors changed their color from light yellow to deep red, which could be easily observed with the naked eye. Because of the highly selective Hg²⁺-promoted deprotection of the dithioacetal, Hg²⁺ converted the protected aldehyde group back to the original aldehyde, and thus the D–π–D structures in S1 and S2 were transformed into D–π–A structures, which accordingly increased the degree of ICT and resulted in an obvious red-shifting of the absorption bands of the compound. Furthermore, the chemosensors could be used for in-field measurements by virtue of a dipstick approach without any additional equipment.

Jiang and co-workers reported a new sensitive probe with a colorimetric and ratiometric response for inorganic and organic mercury species. Upon the addition of Hg²⁺, the absorption peak of the probe shows a considerable red-shift from 370 nm to 439 nm and exhibits an obvious color change from colorless to jade-green. Simultaneously, the fluorescent peak shifts from 472 to 541 nm. The detection limit was ca. 4.9 nM with a linear range of 0–2.5 μM. The action mechanism was attributed to the release of the target sensor with an electron-donating amino group based on a mercury triggered cleavage reaction under mild conditions (Fig. 4b).

Thamaraj and co-workers illustrated an efficient colorimetric chemosensor for Hg²⁺ containing 5-(dimethylamino)-N-(2-mercaptophenyl)naphthalene-1-sulfonamide via a twisted intramolecular charge transfer (TICT) mechanism. It shows a visible color change from colorless to gray upon Hg²⁺ binding, as shown in Fig. 4c. Upon the addition of Hg²⁺, TICT from the electron-rich group (N,N'-dimethylamino group) to the electron-withdrawing group (thiophenol ring with sulfonamide group) takes place because of the interaction between the probe molecule and Hg²⁺ with a complex stoichiometry of 1 : 1. The detection limit is as low as 5.0 × 10⁻¹⁰ M, with a large linear range of 5.0 × 10⁻¹⁰ to 5.0 × 10⁻⁸ mol L⁻¹.

Ermakova and co-workers demonstrated, for the first time, water-soluble anthraquinone-based chemosensors with hydrophilic diethoxyphosphoryl binding groups for the low-cost, rapid, sensitive, and highly selective detection of Hg²⁺ in aqueous solutions. The rapid and steady-going semiquantitative determination of Hg²⁺ was sensitive with a detection limit as low as the ppm level and an linear colorimetric range of 100–1000 ppm. Because of very weak basicity and high absorptivity in the visible region, the target dye can be used for the direct colorimetric determination of Hg²⁺ in water over a wide concentration range, without the need of any buffering medium.

Liu and co-workers reported a simple and highly selective colorimetric sensor bearing a thiosemicarbazide moiety as the binding site and a nitrophenyl moiety as the signaling group (Fig. 4d). When Hg²⁺ was added to a dimethyl sulfoxide (DMSO) solution of the sensor, a dramatic color change from brown to colorless can be observed with a naked-eye detection limit of 5.0 × 10⁻⁸ M Hg²⁺. The highly selective recognition mechanism of the sensor toward Hg²⁺ was based on its ability to form a stable 1 : 1 complex with Hg²⁺ using its C=S and C=O groups. In the complex, charge transfer from the Hg to the N-H end leads to the fading of color. The mechanism was further confirmed and applied for the colorimetric detection of Hg²⁺ using a thiourea moiety as the binding site and a nitrophenyl moiety as the signal group by Lin and co-workers.

Udhayakumari and co-workers reported a highly sensitive and selective detection of Hg²⁺ based on salophen. By the addition of 20–200 μL of Hg²⁺, the color of the sensor system obviously changed from yellow to colorless with a detection limit of 1.0 μg L⁻¹. The reason for the change may be that Hg²⁺ could coordinate with the imine and hydroxyl groups through N, O, and N and O binding sites to form a 1 : 1 complex. The imine in the sensor possessed borderline basic characteristics, and thus it can preferentially bind with Hg²⁺ over Cu²⁺. This was further confirmed by the observation that the corresponding imine without NO₂ substitution in the sensing molecule easily binds Cu²⁺ ions, a borderline acid, with the receptor selectively over Hg²⁺.

For the first time, Kavitha, et al., developed a naturally existing and unmodified simple chemosensor, 2-hydroxy-1,4-naphthoquinone (2HQN), for the colorimetric detection of Hg²⁺ in an aqueous solution of β-cyclodextrin (β-CD). The sensors selectively detected Hg²⁺ via the stable 1 : 1 complexation with Hg²⁺ accompanied with a noticeable color change.

![Image](https://via.placeholder.com/150)
from yellow to colorless. Combined with β-CD, the ability to detect Hg^{2+} could be reached as low as ~10^{-9} M in water. Thus, the detection of Hg^{2+} using this inclusion complex has been demonstrated to be considerably satisfactory. Other organic dye-based colorimetric sensors, which exhibited the mechanism of the formation of sensor–Hg^{2+} chelating complexes to result in obvious color changes, were continuously designed and reported.\textsuperscript{51-60} Many of them possessed a good selectivity, excellent sensitivity and low detection limit, observable by the naked eyes. Thus, it is considered that organic colorimetric sensors have good potential for the practical low-cost detection of Hg ions.

3. Complex based sensors

3.1 Ruthenium complexes containing NCS ligands

It is well-known that Hg^{2+} (a soft acid) can preferentially interact with sulfur (a soft base) according to Pearson’s hard and soft acids and bases theory. Sulfur-containing ligands, in general, have a high affinity for Hg^{2+}, and they are well known to be effective hosts for Hg^{2+}. Accordingly, Coronado et al.\textsuperscript{61} developed two colorimetric sensors for Hg^{2+} detection based on the ruthenium complexes N719 [bis(2,2’-bipyridyl-4,4’-dicarboxylate) ruthenium(II)] bis(tetrabutylammonium)bis(thiocyanate)] and N749 [2,2’,6,2”-terpyridine-4,4’,4”-tricarboxylate] ruthenium(III) tris(tetrabutyl ammonium) tris(iso-thiocyanate)], respectively. Hg^{2+} can reversibly coordinate to the sulfur atom of the NCS groups in the dyes to induce a colour change from dark red-purple to orange with the detection limits ca. 20 ppb using N719 and ca. 150 ppb using N749. Moreover, if the sensor molecules were adsorbed onto high specific surface area mesoporous metal oxide films, i.e., mesoporous TiO\textsubscript{2} films, the reversible heterogeneous sensing of mercury ions in aqueous solution could be obtained by washing with an aqueous solution of KI, which presumably removed the mercury from the surface by forming a stable iodide complex. Subsequently, Censo et al.\textsuperscript{64} confirmed the spectral change of the N719-based complex after adding two equivalents of HgCl\textsubscript{2}. This suggests that the two NCS ligands in the N719 complex are individually bound to one Hg^{2+}.

Different from the abovementioned mechanisms, Palomares et al.\textsuperscript{65} reported a colorimetric sensor using a N719 sensitized mesoporous TiO\textsubscript{2} film to detect Hg^{2+} in a sub-micromolar concentration in aqueous solutions at room temperature. Under the optimized conditions, the “naked eye” detection was found to be as low as 20 nM of Hg^{2+} with the colour change of the film from red-purple to yellow. They confirmed that the colour change can be attributed to the loss of the sulphur atoms from the complex instead of forming a complex with Hg^{2+}.

3.2 Boron complexes

A high performance colorimetric probe for Hg^{2+} generally possesses chromophores with high UV-visible absorptions and specific mercury-coordinating receptors. Yuan et al.\textsuperscript{66} developed a new class of colorimetric probes for the detection of Hg^{2+} by combining boradiazaindacenes as the chromophores, and two crown ether ligands with specific recognition ability for Hg^{2+} ions (Fig. 5). Upon Hg^{2+} addition, a visible colorimetric change from purple to red-pink can be realized on the basis of tuning the photoinduced electron transfer (PET) and intramolecular charge transfer (ICT) processes on a single molecule, which made it possible for the “naked-eye” Hg^{2+}.

Another boron-dipyromethene trimer for Hg^{2+} sensing, containing a benzo[2,1,3]thiadiazole bridge as a receptor for Hg^{2+}, was designed by Sun, et al.\textsuperscript{67} The coordination of Hg^{2+} to the lone pair of electrons on the sulfur atom of the benzo[2,1,3] thiadiazole unit can influence the energy level of the molecular orbitals, inducing an evident change in solution color from purple to yellow with a Hg^{2+} detection concentration as low as 0.5 μM.

Vedamalai et al.\textsuperscript{68} reported a monostyryl boron dipyromethene-based colorimetric chemosensor containing two triazole units for Hg^{2+} detection with a detection limit of 0.226 μM. They illustrated that Hg^{2+} binding mainly occurs through the nitrogen at the triazole ring with a 1 : 1 ratio for the dye–Hg^{2+} complexes, which inhibited the intramolecular charge transfer from nitrogen to boron atom, resulting in a color change from blue to purple. This boron dipyromethene-based Hg^{2+} chemosensor also provided an effective method for Hg^{2+} sensing in a live cell imaging.

3.3 Other metal complexes

Other kinds of complex-based colorimetric sensors have also been designed and applied for Hg^{2+} detection. For example, a series of Pt^{2+} terpyridine complexes featuring an amino-stibene donor–acceptor framework was synthesized for the colorimetric analysis of Hg^{2+} by Chung, et al.\textsuperscript{69} In the presence of Hg^{2+}, the initial interaction between Pt^{2+} and Hg^{2+} would initially lead to the formation of a weak Pt^{2+}···Hg^{2+} bond, followed by a Hg^{2+} –dithiaazaacrown interaction. In addition to the abovementioned co-ordination effects, the strong ICT effect from the dithiaaza-crown to terpyridine could reinforce the possible donor (Pt^{2+}) to acceptor (Hg^{2+}) interaction as shown in Fig. 6a. The optical output could be modulated by switching off the ICT transition upon Hg^{2+} binding and converted to a colorimetric response from the metal-to-ligand charge transfer transition (MLCT). The possible dispersive Pt^{2+}···Hg^{2+} interaction was proposed to rationalize the observed unusual spectral properties at low concentrations of Hg^{2+} in solution. This result might contribute not only to the design of new Hg^{2+} probes but also to the
development of a model system to explore metallophilic interactions.

An iridium(III) bis-cyclometalated complex with a bis(diphenyl-thio-phosphoryl)amide auxiliary ligand was synthesized and applied for Hg\(^{2+}\) detection by Tong, et al.\(^{68}\) The interaction between Hg\(^{2+}\) and the S atom in the bis(diphenylthiophosphoryl)amide ancillary ligand resulted in the dissociation of the ancillary ligand from the complex, accompanied with a color change from orange to light yellow with a detection limit as low as 10\(^{-6}\) M. As shown in Fig. 6b, the ratio of the Ir\(^{3+}\) bis-cyclometalated complex responding to Hg\(^{2+}\) was determined to be 1 : 1. This work demonstrated that phosphorescent probes based on Ir\(^{3+}\) complexes can be realized by using auxiliary ligands containing S atoms.

Ferrocene is a widely used “building block” for constructing sensors, which show potential shifts upon interactions with guest species. For example, Zapata et al.\(^{69}\) developed a ferrocene-quinoxaline dyad to detect Hg\(^{2+}\). Because of the proximity between the metal-ion binding sites on the quinoxaline ring and the ferrocene redox-active moiety, the molecule easily formed a complex with Hg\(^{2+}\) at a 1 : 1 stoichiometry. Upon the addition of Hg\(^{2+}\), an anodic shift of the ferrocene/ferrocenium oxidation peaks and a progressive red-shift (\(\Delta \lambda = 140\) nm) of the low-energy band can be observed accompanied by a color change from orange to dark green with a detection limit of 1.3 \(\times 10^{-5}\) M.

Condensing the H\(_2\)N(\(R\))NH\(_2\) amine with the carbonyl group of ferrocenyl aldehyde, Uahengo et al.\(^{70}\) prepared some Schiff base ferrocene-based conjugated complexes as high sensitive colorimetric sensors for determining Hg\(^{2+}\). Upon the addition of Hg\(^{2+}\), the dramatic naked eye detectable color changes were observed from yellow to red with a limit of detection of 1 \(\mu\)M at ambient temperature. The detection mechanism can be attributed to the coordination of Hg\(^{2+}\) with the \(\pi\)-conjugated system of the sensor. The variation in the conjugated system consequently affects its optical property due to the distance and the path change, thus resulting in different spectral behaviors upon the addition of Hg\(^{2+}\).

### 4. Polymer based sensors

#### 4.1 Natural polymer based sensors

Some natural polymers, such as nucleic acids, proteins and cellulose, are rich in nitrogen, oxygen and sulfur, which can easily form strong coordination bonds with heavy metal ions resulting in changes in their stereo conformations and optical properties. In recent years, various DNA-based selective detection methods for Hg\(^{2+}\) have been developed based on the fact that Hg\(^{2+}\) can specifically bind to the thymine-thymine (T-T) base pair in a DNA duplex. For example, Li et al.,\(^{71}\) for the first time, utilized the Hg\(^{2+}\)-mediated T-T base pair to modulate the folding of G-quadruplex DNAs and inhibited the DNAzyme activity, and thus established a Hg\(^{2+}\) sensing method. As shown in Fig. 7a, two bimolecular DNA G-quadruplexes containing many T residues, which function well in low- and high-salt conditions, respectively, were able to bind with hemin to form the peroxidase-like DNAzymes in the folded state. On the addition of Hg\(^{2+}\), the proper folding of G-quadruplex DNAs is inhibited due to the formation of a T–Hg\(^{2+}\)–T complex. As a result, a sharp decrease in the catalytic activity toward the oxidation of 2,2’-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) by H\(_2\)O\(_2\) is observed, accompanied with a change in color. Using this facial approach, aqueous Hg\(^{2+}\) can be detected at a concentration of 50 nM with the naked eye. The work also provides insights into mercury toxicity in the human body.

The results and mechanism were further confirmed by Lu, et al.\(^{72}\) by integrating polyT sequences for highly selective Hg\(^{2+}\) recognition and two flanking G-quadruplex halves for allosteric signal transductions. The sensor could cost-effectively detect Hg\(^{2+}\) with a detection limit of 4.5 nM because of the interaction between Hg\(^{2+}\) and the T–T mismatches in the polyT sequences.
In regards to the applications of another important natural polymer, cellulose, Xu et al.73 reported that the incorporation of spirolactam rhodamine derivatives on the surface of cellulose filter papers can be applied for the detection of Hg2+ in aqueous media. In the presence of Hg2+ ions, the spirolactam rhodamine derivatives transformed into the ring-opening forms and produced a rapid and specific fluorescence turn-on response with a remarkably enhanced fluorescent emission intensity and clear color change from colorless to pink on complexation with Hg2+ ions. Thus, with a detection limit of 5 × 10−8 M, this functionalized filter paper opened a new way for disposable solid-state sensors for the fluorescent and “naked-eye” detection of Hg2+.

Zhang, et al.74 reported another reversible cellulose based colorimetric Hg2+ sensor by immobilizing a ruthenium dye monolayer onto titania ultrathin gel film pre-coated cellulose nanofibres of a bulk natural cellulose substance (Fig. 7b). The resultant sensing material shows excellent selectivity and sensitivity, and gives a fast and obvious color change from purple to orange in the presence of Hg2+ in aqueous solution with a naked eye detection limit of ~10 ppb.

4.2 Synthetic polymer based sensors

In 2009, Tang et al.75 reported conducting polymer-based chemosensors on Cu2+ with good sensitivities and proposed the concept of the “molecular wire effect”. Our previous work also confirmed the effect with a functional polycetylene containing quinolone-based heterocyclic azo pendants to sense the F− ion.76 For Hg2+ detection, Cheng, et al.77 designed a series of ICT molecules by attaching various electron-donating thiophenes groups to a triphenylamine backbone with an aldehyde group as the electron acceptor. Taking advantage of the distinct Hg2+-promoted deprotection reaction of the dithioacetals, the corresponding dithioacetals were prepared to serve as novel dual-channel chemosensors for Hg2+ with a detection limit as low as 15 μM. Their results further confirmed the molecular wire effect of the conjugated polymers, which endowed the conjugated polymers with excellent sensing performances over those of the corresponding monomers.

Another synthetic polymer incorporating the benzo[2,1,3]thiadiazole moiety as a ligand was developed as a colorimetric and fluorometric sensor for Hg2+ detection in a tetrahydrofuran solution by Ma et al.78 A distinct color change of the polymer-based sensor is observed from orange to colorless with a detection limit of 1.0 × 10−7 M for Hg2+ in a wide proportional range from 0 to 19.0 × 10−5 M. The action mechanism was attributed to the reduction of the π-conjugated system induced by the co-ordination of the S atom of the sensor with Hg2+. These investigations open a way to develop highly effective transitional-metal-sensitive chemosensors by incorporating the benzothiadiazole group in the polymer main-chain backbone.

Satapathy et al.79 designed a thieno-imidazole based polymer sensor [Fig. 8a], with neighboring nitrogen and sulfur heteroatoms as chelating sites for Hg2+. The sensor showed both colorimetric and ratiometric detections of Hg2+ with the color of the polymer solution changing from colorless to yellow via the chelation of the metal ions to both the “S” and “N” heteroatoms.

Recently, Wang et al.80 fabricated a fluorescent sensing film for Hg2+, in which a rhodamine-cyclodextrin fluorophore moiety was loaded on a cross-linked adamantane functionalized nanofiber surface via host-guest interactions (Fig. 8b). Upon the addition of Hg2+, an obvious colour change from white to pink-red was observed with a detection limit of ca. 6.0 × 10−5 M with an efficient proportional range of 1.0 × 10−5–2.0 × 10−4 M. The fact that the N atom of spirolactam would react with the C atom of thiourea results in the ring opening of the spirolactam in rhodamine, followed by the removal of HgS causing an intramolecular guanylation. Thus, a stable cyclic product is formed through an irreversible desulfurization reaction.

5. Nanoparticle based sensors

5.1 Silver nanoparticles

Silver nanoparticles (Ag NPs) have been widely utilized in environmental monitoring with a high sensitivity, good selectivity and biocompatibility because of their intense surface plasma resonance (SPR) bands.81 Certain Ag NPs-based colorimetric sensors have been successfully applied to probe Hg2+ based on the Hg2+-induced aggregation of functionalized Ag NPs, which results in a colour change and UV-vis spectral response.

For instance, Wang et al.82 reported a sensitive and selective colorimetric detection method for Hg2+ based on mercury-specific oligonucleotides (MSO), in which the conformations change from random coils to hairpin structures on the addition of Hg2+. The linear range of the detection was in the range of 25–500 nM with a low detection limit of 17 nM. As shown in Fig. 9a, the presence of Hg2+ would lead to the formation of stable thymine(T)–Hg2–thymine(T) bonds, transforming the random coil MSOs into rigid stem-loops. The Au NPs can no longer bind to the MSO bases and would gradually aggregate together accompanied with a colour change from yellow to red.

Roy et al.83 developed an Ag NPs-based Hg2+ sensor using riboflavin (R) as a reducing and stabilizing agent via a “turn off”–“turn on” mechanism in an aqueous medium. As shown in Fig. 9b, riboflavin is under a ‘turn off’ condition when it binds with the Ag NPs. Upon adding Hg2+, the formation of the strong T–Hg2+–T bond freed the Ag NPs and converted the system to a
'turn on' condition with an immediate colour change from deep orange to bright yellow. The time of sensing was only 1.0 min and the minimum concentration of Hg$^{2+}$ that could be detected was as low as 5 nM.

Wang et al.$^{44}$ reported a dual functional colorimetric sensor for Hg$^{2+}$ detection based on the catalytic reduction of Hg$^{2+}$ to elementary Hg using Ag NPs in the presence of H$_2$O$_2$ (Fig. 9c). In the presence of Hg$^{2+}$, Ag NPs would aggregate and show a colorimetric response from light yellow to deep yellow. This method provided an innovative real-time sensor for trace Hg$^{2+}$ with a detection limit of less than 1 min with a detection limit of less than 2 nM.

Farhadi et al.$^{85}$ illustrated that the redox reaction between biologically synthesized Ag NPs and Hg$^{2+}$ can be applied for the colorimetric recognition of Hg$^{2+}$ in aqueous medium. Fresh biologically synthesized Ag NPs were yellowish-brown in colour due to their intense surface plasmonic resonance absorption band. On contact, Hg$^{2+}$ removed the biological stabilizer compounds that were originally surrounding the Ag NPs. The redox reaction between the Ag NPs and Hg$^{2+}$ further lead to a colour change from yellow to colorless with a detection limit of 2.2 $\times$ 10$^{-6}$ M and a linear range from 10 $\mu$M to 100 $\mu$M.

Tao et al.$^{46}$ for the first time, described the use of the poly(acrylic acid)-templated silver nanoclusters (PAA-AgNCs) as a novel platform for highly sensitive and selective colorimetric sensors for Hg$^{2+}$. On the addition of Hg$^{2+}$, PAA-AgNCs gave a rapid colour change from purple to pale red (Fig. 9d) in less than one minute with a detection limit of 2 nM.

By combining the use of lab-on-paper methodology with nanoparticle science, Apilux et al.$^{87}$ effectively developed a paper-based device decorated with Ag NPs and Ag nanoparticles (Ag NPs) for the simple and rapid detection of Hg$^{2+}$. In the presence of Hg$^{2+}$, the color of the paper immediately changed from yellow to light yellow. The linear detection range was 5–75 ppm with a limit of detection of 0.12 ppm. This color change was attributed to the changes in the surface plasmonic resonance of the AgNPs/AgNPs with their particle size. The resulting paper-based device made it possible for Hg$^{2+}$ measurement with only 2 $\mu$L of sample.

Chen et al.$^{88}$ developed a colorimetric sensor for Hg$^{2+}$ based on the Hg$^{2+}$-induced morphological changes in 1-dodecanethiol-capped Ag NPs in the presence of iodide. As shown in Fig. 9e, Hg$^{2+}$ binds with the thiol molecules, and thus removes them from the Ag NPs. The silver atoms on the surface of the Ag NPs then formed complexes with the dissolved iodide ions. Thus, a color change from blue to purple occurred with a detection limit of 3.3 nM and a good linear relationship from 10 to 500 nM.

Further, Rastogi et al.$^{89}$ prepared label free Ag NPs for Hg$^{2+}$ colorimetric detection in aqueous solutions. Using gum kon-dagogu (GK) as both the reducing and stabilizing agent, the resultant GK reduced/stabilized Ag NPs (GK-Ag NPs) could be directly used for determining Hg$^{2+}$ without any further modification, accompanied by a bright yellow color to colorless. The limit of quantification for Hg$^{2+}$ was as low as 4.9 $\times$ 10$^{-8}$ mol L$^{-1}$ (50 nM) with a linear range of 50–900 nM (R$^2 = 0.998$). The proposed sensing mechanism is based on the redox reaction between the AgNPs and Hg$^{2+}$ in solution.

5.2 Gold nanoparticles

Recently, gold nanoparticles (Au NPs) have attracted considerable attention in the colorimetric detection of metal ions because of their high extinction coefficient over the visible spectrum, tunable surface plasmonic resonance and special surface molecular conjugation features. Various Au NPs-based colorimetric chemosensors for detecting metal ions have been proposed, whose basic strategies are attributed to manipulating the Au NPs with different recognition units such as oligonucleotides, DNAzymes, peptides and proteins, and small thiolate ligands to induce aggregation, thus resulting in a color change.

5.2.1 Nucleotide-functionalized Au NPs. The strong specific interaction of oligonucleotides with Hg$^{2+}$ can selectively bind two DNA thymine (T) bases to form stable T-Hg$^{2+}$-T base pairs, making the oligonucleotides ideal tools for selectively detecting Hg$^{2+}$ in a mixture of analytes. By exploiting this property, different AuNPs-based colorimetric Hg$^{2+}$ sensors have been designed.$^{90-95}$

For example, Lee et al.$^{15}$ reported two types of Au NPs, each functionalized with different thiolated-DNA sequences, i.e., A: 5’HS-C$_{10}$A$_{10}$T-A$_{10}$T and B: 5’HS-C$_{10}$T$_{10}$T-A$_{10}$T, which were complementary except for a single T-T mismatch (Fig. 10a). In the presence of Hg$^{2+}$, the T-T mismatch is bridged by the T-Hg$^{2+}$-T link and the Au NPs aggregate to give a purple-to-red color change at a specific temperature, which is referred to as the melting temperature ($T_m$), depending on the concentration of Hg$^{2+}$. This method provides a low Hg$^{2+}$ colorimetric detection limit of ca. 100 nM.

Using DNA/NP conjugates and T-Hg$^{2+}$-T coordination chemistry, Xue et al.$^{96}$ further developed an Hg$^{2+}$-sensing system at room temperature in a single step. As shown in Fig. 10b, in the absence of Hg$^{2+}$, the DNA decorated NPs do not form aggregates below the $T_m$ because of the T-T mismatch. However, in the presence of Hg$^{2+}$, a clear red-to-purple/pinkish colorimetric response occurs within 5 min due to particle aggregation because of the formation of the T-Hg$^{2+}$-T bridge. The Hg$^{2+}$ detection limit for the 14 nm NP system by the naked
eye is about 3 μM and the sensitivity of the system can be further improved by using larger particles or varying the oligonucleotide sequences on the surface of the nanoparticles. The method also provides rational approaches for detecting other metal ions using the metal-dependent synthetic artificial bases. Importantly, by controlling the sizes of the nanoparticles or by varying the oligonucleotide sequences on the surface of the nanoparticles in the system, the $T_m$ of the target probes can be precisely modulated within a specific range.

Using the polythymine oligonucleotide T$_{33}$, citrate-capped Au NPs and phosphate-buffer saline (PBS) in the presence of Mn$^{2+}$, Yu et al. $^9$ presented a simple and rapid colorimetric assay for Hg$^{2+}$ in aqueous solution (Fig. 10c). The addition of Mn$^{2+}$ to the solution containing 0.75 nM T$_{33}$-AuNPs and 0.2× PBS resulted in an acceleration of the analysis time (within 5 min) and a 10-fold sensitivity improvement for the detection limit of Hg$^{2+}$, which was as low as 10 nM with a linear range from 10.0 nM to 300.0 nM. The authors explained that the Hg$^{2+}$-induced aggregation of the T$_{33}$-Au NPs was accelerated because Mn$^{2+}$ can stabilize the folded structure of the Hg$^{2+}$-T$_{33}$ complex. In addition, Wu et al. $^9$ reported mercury-specific DNA (MSD)-functionalized Au NPs for the colorimetric sensing of Hg$^{2+}$, which relied on measuring the changes in the inhibition of the “non-crosslinking” aggregation of AuNPs induced by the folding of the MSD strand through the T–Hg$^{2+}$–T coordination. As shown in Fig. 10d, the AuNPs functionalized with only one thiolated-MSD sequence (5'-HS-C$_{10}$TCATGTGGTGGCCCTTCTTTCTTA-3'), could specifically interact with Hg$^{2+}$ and form the folding structure via the T–Hg$^{2+}$–T bridges. In the absence of Hg$^{2+}$, the rapid aggregation of Au–MSD occurs, with a color change from red to purple, under a chosen salt condition due to the significant decrease of the inter-particle electrostatic repulsion (Fig. 10d(i)). In the presence of Hg$^{2+}$, the formation of Hg$^{2+}$-MSD complexes on the Au NP surface (designated as Au–MSD–Hg) stabilizes the Au NPs and inhibits the salt-induced aggregation of Au–MSD under the same condition (Fig. 10d(ii)). Thus, this system was ideally suited to be a colorimetric sensor for detecting Hg$^{2+}$ in aqueous solution in the concentration range of 0.1–10 μM of Hg$^{2+}$ with a detection limit of 60 nM.

5.2.2 Thiol-functionalized Au NPs. It is well known that Hg$^{2+}$ is apt to interact with thiols, such as cysteine, protein, and other mercapto derivatives. This property has been exploited for developing colorimetric assays for Hg$^{2+}$ detection based on the strong interaction between thiol-functionalized noble metal nanoparticles and Hg$^{2+}$. For example, Yu et al. $^{10}$ reported a method for sensing Hg$^{2+}$ in salt solutions using Au NPs decorated with 3-mercaptopropionate acid (MPA). The resultant Au NPs could efficiently disperse in salt solutions because of the high negative charge density of MPA on each Au NP surface. Upon the addition of Hg$^{2+}$, the Au NPs aggregated because of the coordination between the carboxylic groups of MPA and Hg$^{2+}$ via the bridging of neighboring NPs and the decrease in the zeta potential on each Au NP. As a result, the color of the solution changed from red to purple with the lowest detectable Hg$^{2+}$ concentration of 500 nM.

Chai et al. $^{11}$ found that cysteine modified AuNPs could be induced to quickly aggregate in the presence of Hg$^{2+}$, especially with the assistance of ultraviolet radiation (Fig. 11a). The aggregation would lead to a substantial red-shift in the plasmon band energy and a red-to-blue color change. The detection of Hg$^{2+}$ can be realized by the naked eye with a detection limit of 100 nM, and can be effectively applied for on-site and real-time Hg$^{2+}$ detection.

Tan et al. $^{12}$ demonstrated, for the first time, that the cloud point extraction of Au NPs modified with MPA and homocysteine (HCys) can be applied for the visual and colorimetric detection of Hg$^{2+}$ in the presence of 2,6-pyridinedicarboxylic acid (Fig. 11b). Unlike most of the Au NP-based methods for sensing Hg$^{2+}$, which involved a colour change from red to blue through the analyte-triggered aggregation of Au NPs, this
method was based on the colour change from colorless to red, which was caused by the transfer of Hg$^{2+}$ associated Au NPs into a surfactant-rich phase. The association of Hg$^{2+}$ with AuNPs enhanced the hydrophlicity of the probe, and thus triggered the transfer of the probe into the hydrophobic surfactant-rich (TX-114) phase. Taking advantage of the selective enrichment function of the cloud point extraction and the colour change of the TX-114-rich phase from colorless to red, Hg$^{2+}$ was determined in a linear range of 2–100 ppb with a detection limit of 2 ppb. This methodology provided an ultrahigh sensitivity and provided new concept for the detection of other metals using suitably functionalized AuNP as probes.

Liang et al.\textsuperscript{110} also illustrated a strategy for Hg$^{2+}$ detection based on the disassembly of L-cysteine-modified Au nanorods (NRs). As shown in Fig. 11c, thiol-contained L-cysteine was selectively bound to the surface of the Au NRs, which induced the aggregation of the Au NRs through a cooperative electrostatic interaction, due to which the colour of the solution of the Au NRs changed from blue-green to gray dark. In the presence of Hg$^{2+}$, cysteine favourably bound with Hg$^{2+}$ over Au, which, in turn, caused the disassembly of the modified Au NRs and the colour of the solution returned to blue-green. The mechanism was considerably different from that of the usually analyte-induced Au NRs aggregation methods. Moreover, the method conveniently enables Hg$^{2+}$ detection with the naked eye within a linear response over 0.5 to 250 μM of Hg$^{2+}$ concentration range with a detection limit of 0.06 μM because the human eye is more sensitive to blue-green than to gray light.

Recently, Zhou et al.\textsuperscript{111} developed a colorimetric sensor for Hg$^{2+}$ in aqueous solutions based on the fact that Hg$^{2+}$ could inhibit the aggregation of Au NPs induced by 4-mercaptophenylboronic acid (MPBA). Without Hg$^{2+}$, MPBA binds to Au NPs via Au–S bonds and induces the aggregation of Au NPs through the self-dehydration condensation of boronic acid groups, with a color change of the solution from red to blue. Because of the higher affinity of Hg$^{2+}$ toward thiolates than AuNPs, in the presence of Hg$^{2+}$, the thiol group of MPBA preferentially binds to Hg$^{2+}$ and the AuNPs disperse again, with a solution color change from blue to red. The absorption ratio ($A_{520}/A_{600}$) was efficiently linear with Hg$^{2+}$ in the range of 0.01–5 μM with a low detection limit of 8 nM (S/N = 3).

Further, Maity et al.\textsuperscript{112} prepared water soluble gold nanoparticles functionalized by the dithiocarbamate derivative of calixarene (DTCC-AuNPs) and applied them as colorimetric sensors for Hg$^{2+}$ in aqueous solutions. This sensor selectively detects Hg$^{2+}$ in aqueous solutions with a sharp color change from red to violet, detectable by the naked eye. Under the optimum conditions, the dynamic response linear range for Hg$^{2+}$ was from 0.2 μM to 100 μM with a detection limit of 40 ppb.

Detailed spectroscopic and microscopic studies revealed that the visual color change is due to the assembly of the gold nanoparticles into arrays through the bare surfaces by dipole–dipole interactions as shown in Fig. 11d. The bare surfaces of the gold nanoparticles were generated by the displacement of the calixarene derivative from the surface of the functionalized gold nanoparticles because of the strong complexation between Hg$^{2+}$ and the calixarene derivative.

5.2.3 **Au-amalgam-based sensors.** Because of the fact that the surface of Au NPs exhibits a strong affinity for mercury, metallic Hg deposits on the surface of Au NPs forms a solid amalgam-like structure, which greatly influences the surface plasmonic resonance, the surface molecular conjugation feature and the resultant colloid stability, which can be used for the colorimetric detection of Hg$^{2+}$.\textsuperscript{113} Accordingly, Lin et al.\textsuperscript{114} reported a rapid and homogeneous method for a highly selective detection of Hg$^{2+}$ using Tween 20-modified Au NPs. As illustrated in Fig. 12a, citrate-capped Au NPs modified with Tween 20 are stable under the conditions of high ionic strength without Hg$^{2+}$. However, in the presence of Hg$^{2+}$, citrate ions would reduce Hg$^{2+}$ to form Hg–Au alloys on the surface of the AuNPs, and thus Tween 20 was removed from the NP surface, resulting in Au NPs aggregation with a colour change from red to purple. Tween 20-AuNPs could selectively detect Hg$^{2+}$ as low as 0.1 μM with a linear range of 200–800 nM.

Fan et al.\textsuperscript{115} developed a colorimetric visualization method for the detection of Hg$^{2+}$ at the ppb level in aqueous solution based on the formation of gold nanoparticles through the Hg$^{2+}$-catalyzed HAuCl$_4$/NH$_2$OH reaction. NH$_2$OH is thermodynamically capable of reducing Au$^{3+}$ ions to Au NPs with a colour change from colorless to red. Then, the reaction between HAuCl$_4$ and NH$_2$OH can be accelerated by Hg$^{2+}$ and the speed of the color change increases within a linear range of 10–1000 mM and a detection limit of 10 nM (2 ppb). The results opened up a new possibility of a rapid, easy, and reliable way for the detection of Hg$^{2+}$ in aqueous samples.

Further, using mesoporous silica-coated gold nanorods (MS Au NRs), Wang et al.\textsuperscript{116} designed a non-aggregation-based label-free colorimetric sensor for Hg$^{2+}$ relying on their chemical redox-modulated surface chemistry. MS Au NRs were used to initiate nucleation catalysis to induce efficient Hg$^0$ deposition on their surfaces in the presence of ascorbic acid, which generated an obvious color change from purple to blue green with a detection limit of 7.9 × 10$^{-10}$ M.

Based on the color change of hexadecyltrimethyl ammonium bromide (CTAB)-coated Au NPs in the presence of non toxic ascorbic acid (AA), Jin et al.\textsuperscript{117} developed an eco-friendly Hg$^{2+}$ detection method in water samples, as shown in Fig. 12b. With the formation process of the amalgamation between Hg and Au, the surface plasmon resonance (SPR) absorption wavelength of the NG shifted from long (dark purple) to short (red) wavelengths. The lowest detected concentrations for Hg$^{2+}$ were...
1.0 μM by the naked eye and 30 nM by UV-visible spectroscopy with a linear range of 0–10 μM. The detection scheme based on the SPR property of Au NPs with a mixture of spherical and rod-shaped gold nanoparticles offers an excellent selectivity and good sensitivity.

5.2.4 Protein-functionalized Au NPs. The toxicity of mercury was found mainly due to its high affinity to the thiol (mercapto) groups in proteins, which leads to dysfunction of cellular enzymes. Therefore, protein, a type of natural polymer containing thiol groups, can be used for the detection of Hg^{2+}. According to this working principle, Guo et al. developed a colorimetric method for Hg^{2+} detection using papain-functionalized gold nanoparticles (P-AuNPs, Fig. 13a). The P-AuNPs were effectively used to detect Hg^{2+} in an aqueous solution based on the aggregation-induced color change from red to blue with the lowest colorimetric detection concentration of ca. 4 μM using 13 nm AuNPs as the detection system. Papain, a protein with seven cysteine residues, could selectively bind with Hg^{2+}, decreasing the distance of AuNPs, yielding both a substantial shift in the plasmonic band energy to a longer wavelength and a red-to-blue color change. These results showed that the sensitivity of the detection system was influenced by the pH and the concentration of P-AuNPs and the size of gold nanoparticles, thus larger gold nanoparticles contributed to more sensitive results.

Du et al. reported another colorimetric detection assay for Hg^{2+} using 13 nm Au NPs modified by linear oligopeptides with cysteine (Cys) at both ends as sensors in aqueous solution (Fig. 13b). When the target linear oligopeptides were added, Au NPs are linked and aggregated together giving a color change from red to blue. Upon the addition of Hg^{2+} into the solution, the oligopeptide probes bind to Hg^{2+} instead of the Au NPs and the solution retains the red color of the isolated Au NPs. More importantly, the detection range for Hg^{2+} can be easily adjusted with a flexible detection range (10 nM to more than 100 μM) by using suitable amounts of the oligopeptide. Its mechanism considerably differs from that of the most other assays based on NPs. In other assays, the presence of Hg^{2+} is established by Hg^{2+} induced particle aggregation. However, in this assay, the presence of Hg^{2+} in the solution prevents particle aggregation, which avoids false positives due to spontaneous particle aggregation. On basis of the same mechanism, You et al. further reported a highly sensitive and selective assay for Hg^{2+} with a color change from light blue to red in aqueous solutions using Au/carboxylethyl quaternized cellulose/cysteine conjugates (Au/CEQC/Cys) based on the thiophilicity of Hg^{2+} and Au NPs, as well as the unique optical properties of CEQC-stabilized Au NPs. The assay could selectively detect Hg^{2+} with a detection limit as low as 40 nM in aqueous solutions.

Based on the aggregation size-dependent optical property of poly-γ-glutamic acid (PGA) functionalized Au NPs, Guan et al. developed a PGA functionalized gold nanoparticle system (PGA-Au NPs) for the colorimetric detection of Hg^{2+}. Negatively charged PGA can efficiently self-assemble on the surface of positively charged CTAB-capped Au NPs. In the presence of Hg^{2+}, Hg^{2+} acts as a cross-linking agent for the pairs of the PGA functionalized Au NPs resulting in the aggregation of Au NPs accompanied with a color change from wine red to dark blue, as shown in Fig. 13c. The colorimetric probe is quite sensitive with a linear range of 0.0110–1.0 M by the naked eye and 30 nM by UV-visible spectroscopy. The assay possesses a highly linear response in the range of 0.001–1.0 μM, with a detection limit as low as 2.6 nM. As shown in Fig. 13d, the detection mechanism was explained by the binding of Hg^{2+} with the cysteine caped on the AuNPs so that the sensing AuNPs are not stabilized any more to aggregate.

To further develop a simple and rapid method for the colorimetric detection of Hg^{2+} by biogenic Au NPs, Tripathi et al. prepared AuNPs using the non-pathogenic and agriculturally considerable fungal biomass of *Trichoderma harzianum* (T. harzianum) without any surface modifications. The reduction of Hg^{2+} in the presence of AuNPs causes the aggregation of the particles with an obvious color change from pink-red to greyish blue, and their SPR shifts to a higher wavelength. The assay possesses a highly linear response in the range of 0.001–1.0 μM, with a detection limit as low as 2.6 nM. As shown in Fig. 13d, the detection mechanism was explained by the binding of Hg^{2+} with the cysteine caped on the AuNPs so that the sensing AuNPs are not stabilized any more to aggregate.

5.2.5 Others. Apart from the abovementioned three kinds of Au NPs-based composites, Hirayama et al. demonstrated that Au NPs capped with triethylene glycol ligands, Au:S-EG3, can also be utilized to be a colorimetric probe for the detection of aqueous Hg^{2+} (Fig. 14a). Upon Hg^{2+} addition, the Au–S bonds are broken and lead to the aggregation of the Au NPs. This is the first example of colorimetric sensing with Au NPs utilizing neither inter-particle crosslinking nor a change in the surface charges of the cluster. A new color changing mechanism involving ligand abstraction from a gold surface by Hg^{2+} was proposed.

Cho et al. reported a fluorimetric/colorimetric Hg^{2+} sensor of Au@SiO₂ core/shell nanoparticles, modified with a porphyrin derivative. In the presence of Hg^{2+}, the color of the system changed from red to green within 10 s, and the changes were
almost reversible when treated with ethylenediaminetetraacetic acid (EDTA) with a detection limit as low as 1.2 ppb for Hg^{2+}. The mechanism was explained as a reverse photo-induced electron transfer (PET) when Hg^{2+} was bound to the nitrogen atoms of the porphyrin moiety (which behaves as a PET donor) with a 1 : 1 stoichiometry between the receptor attached to the Au@SiO_{2} core/shell nanoparticles and Hg^{2+}. These findings showed considerable promise for the development of a new category of tailor-made biocompatible systems built by the immobilization of appropriate chromogenic receptors on the surface of another nanomaterial for the study of the biological function of heavy metal toxins.

A simple colorimetric assay with a tunable dynamic range was developed by Chen et al.^{125} for detecting trace Hg^{2+} in aqueous solution based on the coordination of Hg^{2+} to Au NPs-associated 3-nitro-1H-1,2,4-triazole (NTA). As shown in Fig. 14b, NTA stabilized the Au NPs against tris-induced aggregation through the capping of the Au NPs. In the presence of Hg^{2+}, NTA was released from the Au NP surface via the formation of an NTA–Hg^{2+} coordination complex with a 1 : 1 stoichiometry ratio, leading to the aggregation of AuNPs in tris with the solution color changing from wine-red to dark blue with a low detection limits of 7 nM (1.4 ppb) and 50 nM (10 ppb) observed by a spectrophotometer and by direct visualization, respectively. The detection strategy was unique in terms of high sensitivity and excellent selectivity, especially, a tunable dynamic range, which could be easily tuned by adjusting the amount of NTA in the NTA–AuNP probes.

Recently, Du et al.^{126} developed a logic gate based on AuNPs with melamine and Hg^{2+} as the inputs, and devised a secondary application as a colorimetric probe to detect Hg^{2+} based on the coordinating capability of melamine with Hg^{2+}. Only the addition of melamine would generate a positive readout (red-to-blue colour change), with a good linear range of 50–250 nM and a low detection limit of 50 nM. The action mechanism was attributed to the fact that Hg^{2+} was bound to the NTA surface and caused non-radiative electron/hole recombination annihilation.

Xu et al.^{129} reported a magnetic Fe_{3}O_{4}@SiO_{2}–Rho nanoparticle sensor prepared by modifying the surface of silica-coated Fe_{3}O_{4} nanoparticles with N-(rhodamine 6G) lactam-ethylenediamine. The Fe_{3}O_{4}@SiO_{2}–Rho NPs exhibited selective colour change from colorless to orange with a detection limit of 5 μM. Moreover, the functionalized microspheres showed super-paramagnetic properties, which made it easier to separate the nano-composites from the liquid phase by adding an external magnetic field. Their efforts provided a potential magnetic nanomaterial for the simultaneous sensitive detection and removal of Hg^{2+}.

This year, using L-cysteine as a capping or protecting agent, Soomro et al.^{118} developed copper nanoparticles (Cys-CuNPs) as a colorimetric sensor for determining Hg^{2+} in aqueous solutions. Because of the strong affinity of –SH to Hg^{2+}, Hg^{2+} will remove the protective layer of L-cysteine around the Cu NPs and will result in the aggregation of Cu NPs, with a colorimetric change from brick-red to pale yellow, as illustrated in Fig. 15a. Cys-CuNPs possess a considerably high sensitivity and selectivity for Hg^{2+} in the range of 0.5 × 10^{-6}–3.5 × 10^{-6} mol L^{-1} with a detection limit of 4.30 × 10^{-8} mol L^{-1}. The developed sensor is simple and economic compared to those based on the earlier reported precious metal nanoparticles.

Carbon nano-dots, as a new generation of nanozymes, with their peroxidase mimetic activity could catalyze the H_{2}O_{2}
mediated oxidation of tetramethylbenzidine (TMB) into a blue colored cation radical. Cys as a powerful antiradical biomolecule, could successfully impede the cation radical generation and prevent its emergence as the blue colored reaction product. Accordingly, Mohammadpour et al.\textsuperscript{11} reported a label free on-off colorimetric sensor for Hg$^{2+}$ determination based on carbon nano-dots. As illustrated in Fig. 15b, the sensor is under the “on” state because of the oxidation process catalyzed by the CDs when Cys is absent or when it strongly binds to Hg$^{2+}$. However, in the presence of free Cys, the resultant TMB blue colored radicals will be restored to the original colorless TMB molecules via the hydrogen donation process, and the sensor system is under the “off” state. Upon the addition of Hg$^{2+}$ to the TMB/Cys system, the colorimetric signal was noticeably recovered due to the strong binding preference of Cys to Hg$^{2+}$. The present on-off system has a tunable dynamic range, which could be achieved simply by adjusting the Cys concentration. Accordingly, two calibration ranges of 0.00–0.31 μM and 0.00–0.86 μM were obtained when Cys concentration were 5 and 10 μM, respectively. However, when the Cys concentration was adjusted to 5 μM, an excellent limit of detection of 23 nM was achieved. The turn-on sensing mode in this work provides the feasibility to reduce background signals and enhance the system sensitivity.

6. Conclusions

In conclusion, the colorimetric detection of Hg$^{2+}$ has attracted increasing attention to offer qualitative and quantitative information visually and simply by the naked eye without the use of expensive instrumentation and cumbersome laboratory procedures. To present readers with a better understanding on different methods and their mechanisms, in this review, we summarized the development of colorimetric sensors for Hg$^{2+}$ detection as several different categories according to their receptors, such as organic dye-based sensors, complex based sensors, polymer based sensors, and nanoparticles based sensing systems and others. Great progress has been made for the colorimetric detection of Hg$^{2+}$: sensing materials vary from single organic or inorganic compounds to polynary composites, and analytical procedures vary from cumbersome analyses to real-time on-site ones with better and better selectivities and sensitivities. A considerable amount of work can still be done to develop novel sensing composites with excellent synergistic effects to realize the colorimetric detection, enrichment and separation of Hg$^{2+}$ to reduce Hg$^{2+}$, which causes environmental pollutions.

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Notes and references