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Nanomaterial-based optical sensors for mercury ions

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Highlight

- The unique optical properties of nanomaterials made them candidates in the design of optical sensors
- The review summarized the design principles of nanomaterials-based optical sensors for Hg²⁺ detection
- Three kinds of optical nanosensors were included colorimetric assay, fluorometric analysis and SERS detection

Abstract

As one of the most toxic heavy metals, mercury ion (Hg^{2+}) has become a concern focus for its severe threats to environment and human health. As a result, it is of great importance to develop novel methods to realize the recognition and quantification of Hg^{2+} . The past decades witness the development of nanomaterial-based optical sensors for Hg^{2+} detection, showing the benefits of simplicity, rapidity, high sensitivity and selectivity, and cost-effectiveness. The reported methods have allowed the detectability down to nanomolar concentrations or much lower levels, and proved their practical applications for detecting and quantifying Hg^{2+} in synthetic solutions or natural water samples. In this review, we summarize the published innovations in nanomaterial-based optical sensors for the detection of Hg^{2+} according to different sensing strategies, including colorimetric, fluorescent and surface enhanced Raman scattering detection. Moreover, some challenges and significant attempts related to these methods are also discussed.

Keywords: Nanomaterial, Mercury ion, Colorimetric detection, Fluorescent detection, Surface enhanced Raman scattering

Contents

1 Introduction.....	3
2 Nanomaterial-based colorimetric detection of Hg^{2+}	6

1	2.1 Aggregation of nanomaterials	7
2	2.1.1 Aggregation of labeled nanomaterials	8
3	2.1.2 Aggregation of label-free nanomaterials	11
4	2.2 Morphology transition of nanomaterials	14
5	3 Nanomaterial-based fluorescent detection of Hg^{2+}	17
6	3.1 Hg^{2+} -induced aggregation of fluorescent nanomaterials.....	18
7	3.2 Fluorescence energy transfer system.....	20
8	4 Nanomaterial-based SERS detection of Hg^{2+}	21
9	4.1 Direct aggregation of nanoparticles	23
10	4.2 Hg^{2+} induced signal alteration on SERS active and support-assisted	
11	nanomaterials	26
12	5 Conclusions and outlook.....	28
13	Acknowledgements.....	29
14	References.....	29

15

16 **1 Introduction**

17 Mercury ion (Hg^{2+}) is one of the extremely hazardous metal ions which are widely
 18 presented in the ambient air, water, soil and biota [1-3]. Due to its high toxicity and
 19 bioconcentration effect, Hg^{2+} can cause numerous severe negative impacts on human

1 health, such as kidney failure, brain damage, and various cognitive and motion
 2 disorders [4]. Therefore, it is of great importance to research and develop sensitive
 3 sensing strategies for the recognition and detection of Hg^{2+} in biological and
 4 environmental systems. Traditionally reported approaches available to monitor Hg^{2+}
 5 in aqueous samples include atomic absorption spectrometry [5, 6], atomic
 6 fluorescence spectrometry [7-9], inductively coupled plasma-mass spectrometry [10,
 7 11], fluorometry [12-16] and electrochemical analysis [17-22]. Recently, liquid crystal
 8 based sensor system and resonance Rayleigh scattering aptasensor are also be used to
 9 detect Hg^{2+} [23, 24]. However, most of these methods are limited in their extensive
 10 applications because of the use of expensive and bulky instruments, complex sample
 11 pretreatment processes or low sensitivity and selectivity. As a result, it is very
 12 necessary to explore new approaches for determination of Hg^{2+} to overcome the
 13 restrictions of above mentioned methods.

14 With the flourish development of nanoscience and nanotechnology, various
 15 nanomaterials with different morphologies have been successfully synthesized, such
 16 as gold/silver nanoparticles (Au/Ag NPs) [25, 26], gold nanorods (Au NRs) [27],
 17 semiconductor quantum dots (QDs) [28], graphene [29], carbon dots (CDs) [30], etc.
 18 On account of their unique optical properties, nanomaterial becomes an important
 19 optical-translating unit in the construction of optical sensors. Typically, the optical
 20 properties of nanomaterials can be varied via target-induced
 21 aggregation/anti-aggregation or their surface change [31, 32]. By combining with the
 22 recognition unit, such as small molecular ligands, biological macromolecules and

1 specific chemical/biological reactions, the nanomaterial-based optical sensors show
2 specific and selective response to the target molecule. According to the reported
3 design strategies for optical nanosensors in recent years, the most popular sensing
4 techniques include colorimetric detection, fluorometry and surface enhanced Raman
5 scattering (SERS) [33]. Except the function of translating sensing behavior of target
6 into optical signals, the use of these novel nanomaterials can also endow high
7 sensitivity to the proposed nanosensors.

8 Among a variety of target molecules, optical nanosensors for the determination of
9 Hg^{2+} have attracted increasing interest, and numerous related sensors have been
10 constructed. Recently, some excellent reviews on this topic have appeared in special
11 journal issues based on the importance of the usage of nanomaterials [34-37]. Xu *et al.*
12 [34] reviewed the development of different nanomaterial-based approaches for the
13 detection of mercury according to the kinds of nanomaterials, and the speciation
14 analysis of mercury using nanomaterials was also be discussed. Botasini *et al.* [35]
15 critically discussed the applicability of the nanotechnology-based sensors to the
16 analysis of real samples for Hg^{2+} determination. Chansuvarn *et al.* [38] summarized
17 colorimetric and visual assays for determination of Hg^{2+} based on gold-based
18 nanomaterials. The above mentioned reviews offer different perspectives to overview
19 the nanomaterial-based optical sensors, however, a comprehensive summary in the
20 design strategies of optical nanosensors for Hg^{2+} has not been given, especially the
21 fluorometric and SERS detection strategies.

22 In this review, the prominent optical nanosensors for Hg^{2+} are summarized based on

different detection techniques. Firstly, we discuss nanomaterial-based colorimetric detection of Hg^{2+} based on the aggregation and morphology transition of nanomaterials; in the following, fluorescent nanosensors for Hg^{2+} are **overviewed including** Hg^{2+} -induced aggregation of fluorescent nanomaterials and fluorescence energy transfer system; moreover, nanomaterial-based SERS detection is focused on for the detection of Hg^{2+} via direct aggregation of nanoparticles and Hg^{2+} induced signal alteration on SERS active and support-assisted nanomaterials. Finally, the review ends with the conclusions of the latest advances and **outlook** in the development of nanosensors for Hg^{2+} .

2 Nanomaterial-based colorimetric detection of Hg^{2+}

Colorimetric assay is the analytical method which the signal recognition event of the target molecule **can** be transformed into naked-eye sensitive color change. It is extremely attractive in chemical and biological analysis for its advantages of simplicity, rapidity, and cost-effectiveness [39, 40]. Compared with conventional organic chromophores or dyes, the molar extinction coefficients of noble metal nanomaterials, especially gold and silver nanomaterials, are higher in 3~5 orders of the magnitude in the visible region, which is due to their unique localized surface plasmon resonance (LSPR) [41]. For instance, the molar extinction coefficients of Au NPs with 13 nm and 50 nm diameters are $2.7 \times 10^8 \text{ M}^{-1} \text{ cm}^{-1}$ and $1.5 \times 10^{10} \text{ M}^{-1} \text{ cm}^{-1}$ at ~520 nm, respectively [38]. Moreover, The LSPR frequency depends on the material composition, particle size, shape, interparticle distance and dielectric

1 environment [42, 43]. Any change in these parameters can affect the
 2 plasmon-resonance frequency, along with the color change of the nanoparticle
 3 solution. For example, 13 nm Au NPs with wine red color possess a strong absorption
 4 band at a wavelength of about 520 nm, and the aggregation of Au NPs results in a
 5 significant red-shifting in the surface plasmon band, changing the solution color from
 6 red to blue [44]; **similarly**, the morphologic change from dispersed Ag NPs to
 7 aggregated Ag NPs is corresponding to the color change from yellow to brown [45];
 8 Au NRs display two strong absorption **bands** in the visible region, and **their** colors
 9 **depend** on the change of length-diameter ratio [27]. Based on the distinctive optical
 10 properties, gold and silver nanomaterials have become good candidates for **the design**
 11 **of** colorimetric sensors.

12 In recent years, colorimetric detection of Hg^{2+} based on gold and silver
 13 nanomaterials has gained wide attention, and many novel methods have been
 14 successfully applied to detecting trace Hg^{2+} in actual samples. The reported
 15 colorimetric sensors of Hg^{2+} can be divided into two **main** types: one is based on the
 16 target-regulated interparticle distance of nanoparticles (monodisperse or aggregated),
 17 called aggregation based method; the other mainly uses analyte-induced morphology
 18 transition of nanomaterials, which is called morphology transition based method.

19 **2.1 Aggregation of nanomaterials**

20 Indeed, the excellent LSPR properties of gold and silver nanomaterials are strongly
 21 dependent on the interparticle distance, and a decrease of the distance could result in

the coupling of interparticle surface plasmon, along with a red shift in the LSPR band and a visual color change in solutions. This interparticle-distance-mediated color change provides an appropriate platform for colorimetric sensing target molecules which can directly or indirectly trigger the change of interparticle distance of noble metal nanomaterials. According to the modification functional ligands or not, aggregation based colorimetric sensors of Hg^{2+} can be divided into two main types, namely labeled and label-free nanomaterials based aggregation. Table 1 lists some typical examples of aggregation-based colorimetric assay for Hg^{2+} detection [46-71], including the applied nanomaterials, the sensing strategy and the detection performance.

Table 1

2.1.1 Aggregation of labeled nanomaterials

The functionalization of nanomaterials endows aggregation based colorimetric sensors with high sensitivity and selectivity. The main functional group for functionalizing the surfaces of nanoparticles is sulfhydryl group due to the strong Au-S or Ag-S bond, and mercapto derivatives have become the most attractive ligands to modify gold and silver nanomaterials to keep them monodisperse. When Hg^{2+} is introduced, the aggregation of nanoparticles is induced by forming interparticle complexes between the labeled ligands and Hg^{2+} , leading to a distinct color change. Generally, the functional ligands used to detect Hg^{2+} are small organic molecules and oligonucleotides.

One main detection principle of small organic molecules labeled nanoparticles is based on the chelate reaction. For instance, Chen *et al.* synthesized a sulfhydryl compound N-1-(2-Mercaptoethyl)thymine which was used to modify Au NPs by Au-S bond [52]. As schematically shown in Fig. 1A, the obtained functionalized Au NPs could aggregate in the presence of Hg^{2+} by forming a T-Hg-T complex with strong affinity, resulting in an obvious change of color and UV-Vis absorption spectra. The developed method was highly sensitive (2.8 nM) and selective over other metal ions, and successfully applied to detect Hg^{2+} in real water samples. Yu and coworker used 3-mercaptopropionate acid (MPA) and adenosine monophosphate (AMP) decorated Au NPs to realize the detection of Hg^{2+} in a high-salinity solution [47]. Due to the high negative charge density of AMP, the MPA/AMP-capped Au NPs dispersed well in a high-salt solution; however, the aggregation of Au NPs was induced by Hg^{2+} because of the coordination between Hg^{2+} and the carboxylic group of MPA. Under the optimum conditions, the lowest detectable concentration of Hg^{2+} was 500 nM on the basis of the measurement of A_{620}/A_{520} . Moreover, the lowest detectable concentration could be down to 50 nM by modifying MPA/AMP-capped Au NPs with highly fluorescent rhodamine 6G (R6G).

The other detection principle of small organic molecules labeled nanoparticles is Hg^{2+} -induced ligand exchange. Liu *et al.* reported a novel mercury(II)-controlled approach using quaternary ammonium group-terminated thiols modified Au NPs (QA-Au NPs) [48]. As shown in Fig. 1B, QA-Au NPs were well dispersed in acidic aqueous solution due to the electrostatic repulsion between the QA cations and

1 positively charged H^+ . The addition of Hg^{2+} induced the abstraction of ligands from
 2 Au NPs surfaces, resulting in the aggregation of Au NPs for the lack of sufficient
 3 charges or stabilizing agents on Au NPs surfaces. Based on this sensing strategy, a
 4 dynamic detection range was obtained from 3×10^{-8} to 1×10^{-2} M. Liang *et al.*
 5 provided a colorimetric sensor for the detection of Hg^{2+} based on the disassembly of
 6 Au NRs [71]. As depicted in Fig. 1C, L-cysteine was fabricated on the surfaces of Au
 7 NRs via Au-S bond, which caused the assembly of Au NRs through cooperative
 8 electrostatic interaction, accompany with a color change from blue-green to gray dark.
 9 In turn, Hg^{2+} led to the disassembly of the modified Au NRs and the color of the
 10 solution returned to blue-green. This effect enabled the optical determination of Hg^{2+}
 11 with a linear response in the concentration range from 0.5 to 250 μ M, an excellent
 12 selectivity for Hg^{2+} , and high recoveries ranging from 99 to 106% in spiked
 13 environmental water samples.

Fig. 1

15 For oligonucleotides modified nanoparticles, the recognition of Hg^{2+} is realized on
 16 the basis of T- Hg^{2+} -T coordination chemistry. Xu and coworkers proposed a novel
 17 colorimetric method for the detection of Hg^{2+} based on deoxythymidine triphosphates
 18 (dTTPs)-functionalized Au NPs (T-Au NPs) [54], as illustrated in Fig. 1D. The
 19 sensing mechanism of this approach is the specific formation of
 20 mononucleotide/metal complexes induced Au NPs aggregation, causing a significant
 21 hypochromicity of the 520 nm band and a bathochromic shift centered maximum on
 22 680 nm. The colorimetric sensor showed high sensitivity and selectivity, as well as the

1 potential application in tap water and river water. Lee *et al.* developed a colorimetric
 2 detection of Hg^{2+} in aqueous media using DNA-functionalized Au NPs [53]. As seen
 3 in Fig. 1E, two thiolated-DNA sequences (probe A: 5'HS-C₁₀-A₁₀-T-A₁₀3', probe B:
 4 5'HS-C₁₀-T₁₀-T-T₁₀3') with a single thymidine–thymidine mismatch were modified
 5 on the surfaces of Au NPs, respectively. The aggregates of Au NPs melted with a
 6 dramatic purple-to-red color change at about 46 °C. However, the melting
 7 temperatures was higher than 46 °C in the presence of Hg^{2+} because of the strong
 8 coordination of T– Hg^{2+} –T, which **made** up the T–T mismatch. Based on this
 9 mechanism, the limit of detection of approximately 100 nM was obtained.

10 Generally, colorimetric sensors based on the aggregation of labeled nanomaterials
 11 possess high sensitivity and selectivity toward Hg^{2+} . However, this kind methods are
 12 limited by a complicated and time-consuming separation step which is necessary for
 13 the modification of nanomaterials to avoid the recognition between the analyte and
 14 the dissociative ligands.

15 **2.1.2 Aggregation of label-free nanomaterials**

16 Compared with labeled nanomaterials aggregation based colorimetric sensors, the
 17 ones using label-free nanomaterials are more attractive for their time-effective
 18 property. To summarize the present label-free nanomaterials aggregation based
 19 colorimetric sensors, the main measuring principles include Hg^{2+} -induced ligand
 20 exchange, Hg^0 deposition, and T– Hg^{2+} –T coordination chemistry.

21 Hg^{2+} -induced ligand exchange is usually used in small organic molecules mediated

aggregation of gold and silver nanomaterials. In 2014, Duan and coworkers investigated a facile colorimetric method for Hg^{2+} based on the anti-aggregation of Ag NPs [67]. As schematically shown in Fig. 2A, the addition of 6-thioguanine could lead the aggregation of Ag NP through Ag-S bond, accompanying with a red shift of absorption spectra and a color change from yellow to brown. Due to the stronger affinity between 6-thioguanine and Hg^{2+} than that with Ag NPs, Hg^{2+} could restrain 6-thioguanine-induced aggregation of Ag NPs along with a color change from brown to yellow. Under the optimal conditions, the linear response was obtained in the range from 0 to 333 nM. Chen *et al.* proposed a colorimetric nanosensor strategy for the detection of mercury speciation based on the target-induced aggregation of Au NPs with the help of diethyldithiocarbamate (DDTC) [72], as illustrated in Fig. 2B. Because the complex Hg-DDTC was more stable than Cu-DDTC, a displacement between Hg species and Cu^{2+} would occur, resulting in the aggregation of Au NPs with a color change. More importantly, by virtue of the masking effect of ethylenediaminetetraacetic acid (EDTA), the colorimetric sensor could successfully discriminate organic mercury from inorganic mercury. The simple, rapid, and sensitive label-free colorimetric sensor for the determination of Hg species provided an attractive alternative to conventional methods, which usually involve sophisticated instruments, complicated processes, and long periods of time.

The deposition of Hg^0 on the surfaces of nanomaterials might well occur in the presence of reducing agent, such as citrate ions and ascorbic acid (AA). Lin *et al.* developed a rapid and homogeneous colorimetric method for the detection of Hg^{2+} and

1 Ag^+ by using Tween 20-modified Au NPs [73]. As depicted in Fig. 2C, Tween 20
 2 stabilized citrate-capped Au NPs were monodispersed in **solution with** high ionic
 3 strength; citrate ions adsorbed on the Au surfaces could reduce Hg^{2+} and Ag^+ to form
 4 Hg–Au alloys and Ag on the surfaces of the Au NPs, removing Tween 20 from the Au
 5 NPs surfaces. As a consequence, the aggregation of Au NPs was induced in a
 6 high-ionic-strength solution. The proposed method could selectively detect Hg^{2+} and
 7 Ag^+ at concentrations of 0.1 and 0.1 μM in the presence of NaCl and EDTA,
 8 respectively. Afterwards, Lou *et al.* reported a “blue-to-red” colorimetric sensor for
 9 determination of Hg^{2+} and Ag^+ based on Tween 20 stabilized Au NPs by the reduction
 10 of AA [62]. As seen in Fig. 2D, the addition of N-acetyl-L-cysteine induced the
 11 aggregation of stabilized Au NPs in phosphate buffer solution with high ionic strength
 12 for self-assembly of mercapto ligand on the surfaces of Au NPs, exhibiting a blue
 13 color; however, the presence of Hg^{2+} or Ag^+ could be reduced with the aid of AA to
 14 form Hg–Au alloy or Ag coating on the surfaces of Au NPs, blocking the assembly of
 15 mercapto ligand and making the solution in red color. Therefore, a “blue-to-red”
 16 colorimetric sensing strategy could be established for Hg^{2+} and Ag^+ detection.

17 T– Hg^{2+} –T coordination chemistry is another key principle for the detection of Hg^{2+}
 18 in label-free nanomaterials aggregation based colorimetric sensors. Lou *et al.*
 19 proposed a simple and sensitive method for the detection of Hg^{2+} by using
 20 anti-aggregation of Au NPs [57], as illustrated in Fig. 2E. Thymine can bind to Au
 21 NPs through Au–N bond and induced the aggregation of Au NPs. The presence of
 22 Hg^{2+} could ordinate with thymine by forming thymine- Hg^{2+} -thymine coordination

1 complex, inhibiting the aggregation of Au NPs. Based on this sensing strategy, Hg^{2+}
 2 could be detected sensitively and selectively. Qing and coworkers reported a
 3 colorimetric assay for quantifying Hg^{2+} or Ag^+ by using designed unimolecular
 4 multifunctional DNA probe (UMDP) and unmodified Au NPs as sensing element and
 5 color-reporting probe, respectively [60]. (Fig. 2F) When adding Hg^{2+} or Ag^+ , the
 6 UMDP with random coil structure changed into hairpin-like structures with a
 7 T- Hg^{2+} -T or C- Ag^+ -C base pairing, resulting in salt-induced Au NPs aggregation.
 8 Meanwhile, a red-to-blue color change and a red shift of the plasmon band in the
 9 UV-visible absorption spectrum was obtained. The two target ions could be simply
 10 distinguished by using EDTA, since Hg^{2+} could not cause Au NPs aggregation while
 11 Ag^+ ions could still cause the aggregation in the presence of EDTA.

12 **Fig. 2**

13 **2.2 Morphology transition of nanomaterials**

14 As we know, the color-tunable behavior of gold and silver nanomaterials also depends
 15 on their size and shape, which enables them attractive candidates for the design of
 16 optical sensors. For morphology transition based colorimetric sensors, the recognition
 17 of target molecule was realized by a particular analyte-induced surface chemical
 18 reaction, ensuring the high selectivity of the sensor. Currently, the colorimetric
 19 sensors for Hg^{2+} detection based on this sensing strategy are few, and the related
 20 nanomaterials involves Au NPs, Au NRs Ag NPs and silver nanoprisms (Ag NPRs)
 21 [74-78].

Fig. 3

One kind of the morphology transition based colorimetric sensors are designed based on Hg^{2+} -induced etching of nanomaterials. In 2006, Rex *et al.* developed a direct way to monitoring Hg^{2+} based on the well-known amalgamation process that occurs between mercury and gold [74], as illustrated in Fig. 3A. When adding the water sample into Au NRs solution containing the reductant (NaBH_4), the formed amalgamation could deposit more efficiently at the tips of the nanorods, resulting in the decrease of their effective aspect ratio of the nanorods. Meanwhile, the blue shift of the longitudinal absorption band and the color change were also observed. The proposed method was not only easy and rapid (less than 10 min), but also accurate and sensitive (the limit of detection was $6.6 \times 10^{-13} \text{ g} \cdot \text{L}^{-1}$), showing high potential for determining ultralow levels of Hg^{2+} in water samples. Chen *et al.* reported a novel colorimetric sensor for Hg^{2+} detection based on morphology transition of 1-dodecanethiol ($\text{C}_{12}\text{H}_{25}\text{SH}$)-functionalized Ag NPRs [77]. As depicted in Fig. 3B, the presence of $\text{C}_{12}\text{H}_{25}\text{SH}$ could protect Ag NPRs from the etching of iodides (I^-) by the formation of complexation between Ag^+ and I^- . When added Hg^{2+} , the abstraction of $\text{C}_{12}\text{H}_{25}\text{SH}$ from the surfaces of Ag NPRs resulted the consumption of silver atoms from the surfaces of Ag NPRs, leading to the changes in the particle morphology, the color, and UV-vis absorption spectra of colloidal solution. With the increase of Hg^{2+} concentration from 10 to 500 nM, a good linear relationship was obtained and the limit of detection was 3.3 nM. Moreover, the satisfying recoveries were realized over 92% in different real water samples by using the proposed method. Noor and

1 coworkers used graphene oxide-silver (GO-Ag) nanocomposite to realize the
 2 quantitative determination of Hg^{2+} [79]. Due to the higher redox potential of $\text{Hg}^{2+}/\text{Hg}^0$
 3 (+0.85 V) than that of Ag^+/Ag^0 (+0.8 V), Hg^{2+} could oxidize the metallic Ag atoms to
 4 produce Hg atoms and Ag^+ ions. As a consequence, a significant decrease in the
 5 absorption intensity with a blue shift on the SPR band of the Ag NPs was clearly
 6 observed upon increasing the concentration of Hg^{2+} . By using the proposed method, a
 7 linear relationship was obtained in the Hg^{2+} concentration range of 5–75 μM and the
 8 limit of detection was calculated as 0.59 μM .

9 The other kind of the morphology transition based colorimetric sensors are
 10 fabricated based on the formation of nanomaterials or the new shells deposited on the
 11 original nanomaterials. For instance, Fan *et al.* presented a direct way to quantify
 12 Hg^{2+} by the formation of Au NPs, which was realized with the assistance of
 13 Hg^{2+} -accelerated $\text{HAuCl}_4/\text{NH}_2\text{OH}$ reaction [75]. As shown in Fig. 3B, the growth rate
 14 of Au NPs and the speed of color change were proportional to the initial concentration
 15 of Hg^{2+} . The entire procedure took less than 20 min, and the high selectivity and
 16 sensitivity were obtained from the well-known amalgamation process between
 17 mercury and gold. The one-step and label-free colorimetric method had been used to
 18 monitor Hg^{2+} in spiked lake water sample with satisfying recoveries. Wang and
 19 coworkers provided a morphology transition based colorimetric sensing strategy for
 20 Hg^{2+} relying on chemical redox-modulated surface chemistry [76]. Employing
 21 mesoporous silica-coated gold nanorods (MS Au NRs) as an interface for optical
 22 sensing, Hg^{2+} was reduced to Hg^0 by AA, inducing Hg^0 deposition on the surfaces of

MS Au NRs and a distinguish color change of the MS Au NRs. What's more, Hg^0 -deposited MS Au NRs (Hg^0 -MS Au NRs) could be used as an indicator for the detection of S^{2-} , due to S^{2-} and O_2 mediated rapid extraction of Hg^0 from MS Au NRs surfaces within several seconds.

3 Nanomaterial-based fluorescent detection of Hg^{2+}

Fluorescent assay is the method which translates the target recognition information into changeable fluorescence signals. The typical fluorescent sensing system based on organic dyes exhibits high sensitivity and relative versatility; however, the inevitable shortcomings, such as complicated synthesis and modification procedures and poor water solubility, severely limit the practical application of the existing fluorescent methods [80-84]. Fortunately, the developments of nanomaterials become new alternatives for organic dyes in the design of chemical and biological fluorescent sensors. Fluorescent nanomaterials including QDs, CDs and gold/silver nanoclusters (Au/Ag NCs) possess advantages of size-dependent broad absorption, size-tunable emission as well as photochemical stability. These successful preparation of fluorescent nanomaterials has yielded many fluorescence detection systems. Typically, a fluorescence nanosensor consists of two functional units: a fluorescent component for signaling the binding event and a recognition element to provide specific binding with the targets. Based on the fluorescent properties of nanomaterials and requirement of the assay for Hg^{2+} detection, fluorescent nanosensors can be designed as Hg^{2+} -induced aggregation of fluorescent nanomaterials and fluorescence energy

transfer system. Table 2 lists some typical examples of fluorescent assay for Hg^{2+} detection, and the applied nanomaterials, the sensing strategy and the detection performance are included [85-113].

Table 2

3.1 Hg^{2+} -induced aggregation of fluorescent nanomaterials

The aggregation of fluorescent nanomaterials can induce the quenching of their fluorescence, which is the main tactics for the design of the sensor to determine Hg^{2+} .

And the aggregation of fluorescent nanomaterials usually results from the complexation, the replacement of ligands and the T- Hg^{2+} -T coordination chemistry.

For example, Wang *et al.* reported a fluorescent detection of Hg^{2+} by using graphene quantum dots (GQDs) prepared by ultrasonic route [104]. When adding Hg^{2+} , the emission spectrum of GQDs at 430 nm was quenched significantly. Because the surfaces of the as-prepared GQDs were attached with a lot of carboxylate groups, Hg^{2+} might exhibit a certain affinity to the carboxylate groups on the surfaces of GQDs and induce the aggregation of GQDs to some extent. As a consequence, the fluorescence of GQDs was quenched along with Hg^{2+} added into the GQDs solution gradually. Under optimum conditions, the change of fluorescence intensity was directly proportional to the concentration of Hg^{2+} in the range from 8.0×10^{-7} to 9×10^{-6} M with a detection limit of 1.0×10^{-7} M. Similarly, the binding between Hg^{2+} and the carboxylate group on L-cysteine resulted in the aggregation of L-cysteine-capped CdS QDs. And the concentration of Hg^{2+} was in proportion to the

1 quenching amounts of fluorescence [94]. Ke *et al.* used mercaptopropionic acid (MPA)
 2 coated Mn doped ZnSe/ZnS QDs to develop an ultrasensitive and selective
 3 fluorescent sensor for the detection of Hg^{2+} [101], as illustrated in Fig. 4. According to
 4 the strong interaction between Hg^{2+} and thiols, MPA played a key role in the process
 5 of recognizing Hg^{2+} . In the presence of Hg^{2+} , the QDs rapidly aggregated selectively
 6 due to the changes of their surface chemical properties, resulting in dramatic
 7 quenching of fluorescent intensity. Meanwhile, IR analysis was also conducted to
 8 prove the separation of MPA from the surfaces of colloidal nanoparticles influenced
 9 by the strong chelation between Hg^{2+} and thiols. The result showed that the QD-based
 10 metal ions sensor possessed satisfactory precision, high sensitivity (the detection limit
 11 of 0.1 nM) and selectivity, and could be applied for the quantification analysis of Hg^{2+}
 12 in drinking water samples. Using oligonucleotide (5'-ACC CGA ACC TGG GCT
 13 ACC ACC CTT AAT CCCC-3') and NaBH_4 as stabilizer and reducing agent, one-step
 14 synthesized DNA-Ag NCs could also be used to detect metal ions [90]. Because Hg^{2+}
 15 can bind with thymine (T) residues in single-stranded DNA, the interaction between
 16 Hg^{2+} and the oligonucleotides on the surfaces of the nanoparticles probably caused the
 17 aggregation of the DNA-Ag-NCs, which was responsible for the fluorescence
 18 quenching of DNA-Ag NCs. Apart from Hg^{2+} , Cu^{2+} could also quench the
 19 fluorescence of DNA-Ag NCs on account of the specific and strong metallophilic
 20 interaction between Cu and Ag atoms in DNA-Ag NCs. The limits of detection of
 21 Hg^{2+} and Cu^{2+} were 5 nM and 10 nM, respectively. Moreover, the label-free DNA-Ag
 22 NC assay system has been successfully used to sense Hg^{2+} and Cu^{2+} in tap water and

1 spring water.

2 **Fig. 4**

3 **3.2 Fluorescence energy transfer system**

4 Except the Hg^{2+} -induced aggregation of fluorescent nanomaterials systems,
 5 fluorescence energy transfer system is another key choice for the design of fluorescent
 6 sensors. Fluorescence resonance energy transfer (FRET) is a non-radiation process,
 7 and its character is the energy transfers from an excited donor to an acceptor through
 8 longrange dipole–dipole interaction. An efficient FRET process needs to meet two
 9 **requirements**: one is the overlap between acceptor absorption spectrum and the donor
 10 emission spectrum; the other is that the distance between a donor and an acceptor
 11 must be linked in close proximity, typically less than a few nanometers. Due to the
 12 overlap between the green luminescence of the donor (Er^{3+}) and the strong absorption
 13 band of the acceptor (CdTe QDs), a novel FRET sensor with $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$
 14 upconversion nanoparticle (UCNP)/CdTe QDs composite was designed for Hg^{2+}
 15 detection [106]. As depicted in Fig. 5A, the addition of Hg^{2+} led to the quenching of
 16 QDs due to the change of surface states by the binding between carboxyl capping
 17 layer and Hg^{2+} . The sensor showed high selectivity, a low detection limit of 15 nM
 18 and good linear Stern–Volmer characteristics, both in the buffer solution and serum.

19 Similar to FRET, the nanometal surface energy transfer (NSET) is another
 20 mechanism with a high energy transfer rate from the energy donor to the energy
 21 acceptor and a long quenching distance. Li *et al.* used the QD/DNA/Au NP ensemble

1 to design a fluorescent sensor to realize the determination of Hg^{2+} [99]. As seen from
 2 Fig. 5B, two ssDNA strands ($5'$ -HS-CAGTTTGGAC- $3'$ and
 3 $5'$ -HSGTCCTTTCTG- $3'$) were complementary except for three deliberately designed
 4 T-T mismatches and were modified on the surfaces of CdSe/ZnS core-shell QDs and
 5 the 3 nm sized Au NPs, respectively. When the Hg^{2+} was absent, two ssDNA strands
 6 were not capable of hybridization and dispersing in the aqueous solution due to the
 7 electrostatic repulsion from the negatively charged ssDNA attached on the
 8 nanoparticle surfaces. In this case, the CdSe/ZnS QDs could emit fluorescent signal at
 9 572 nm under an excitation laser. In the presence of Hg^{2+} , DNA hybridization would
 10 occur due to the formation of thymine- Hg^{2+} -thymine complexes. Consequently, QDs
 11 and Au NPs would be brought into close proximity, which enabled the quenching of
 12 the fluorescence emission. Based on this principle, the proposed nanosensor exhibited
 13 a limit of detection of 0.4 and 1.2 ppb toward Hg^{2+} in the buffer solution and in the
 14 river water, respectively.

15 **Fig. 5**

16 **4 Nanomaterial-based SERS detection of Hg^{2+}**

17 SERS technique is the method which uses the surfaces of rough metal to enhance the
 18 Raman signals of the adsorbed molecules. During the past decades, various noble
 19 metal nanomaterials based SERS substrates have been reported due to their excellent
 20 enhancement of Raman signals [114]. The elaborated theory of SERS is attributed to
 21 the long-range electromagnetic enhancement (EM) and the short-range chemical

1 enhancement (CE) [115, 116]. SERS detection has received extensive attentions
 2 owing to its in-situ, non-destructive and high-sensitive features, and becomes a
 3 powerful spectroscopy technique in various fields, such as the detection of chemical
 4 and biological molecules [117-120], drug delivery [121-123] and the diagnose and
 5 treatment of disease [124-126].

6 In general, a SERS sensor of Hg^{2+} includes three parts: (1) a metal nanosubstrate,
 7 (2) an organic Raman reporter molecule and (3) a ligand with high specificity toward
 8 Hg^{2+} . Various metal nanostructures with different size, geometry, chemical
 9 composition, and surface chemistry can strongly enhance the Raman signals due to
 10 the local optical fields at metal surfaces. Currently, the widely used nanomaterials are
 11 Au/Ag NPs, Au NRs, gold nanoflowers, and Au–Ag bimetallic NPs. Raman reporter
 12 molecule is another important component which could be attached to noble metal
 13 nanomaterials to generate vibrational spectroscopic fingerprint information. They are
 14 required to have large Raman cross-section and affiliation to noble metal surface
 15 through electrostatic or covalent binding [114]. Typically, some nitrogen-containing
 16 cationic dyes, sulfur-containing dyes, and thio-small molecules can be selected as
 17 Raman reporters. The specific ligand could selectively distinguish Hg^{2+} from other
 18 interfering substances. Table 3 lists a series of nanomaterial-based SERS methods for
 19 Hg^{2+} detection, including the applied nanomaterials, the sensing strategy and the
 20 detection performance [127-145]. According to the reported SERS sensors of Hg^{2+} ,
 21 the sensing strategies can be divided into two kinds: direct nanoparticle aggregation
 22 based SERS nanosensor and Hg^{2+} induced signal alteration on SERS active and

support-assisted nanomaterials.

Table 3

4.1 Direct aggregation of nanoparticles

The design of nanoparticle aggregation based SERS nanosensor is originated from the greatly enhanced electromagnetic field in the hotspots of noble metal NP junctions. The aggregation of noble metal NPs can be formed mainly based on three mechanisms. The first one is based on the stronger binding ability of Hg^{2+} to thiol-containing and nitrogen-containing small molecules. For example, Li *et al.* reported a “turn off” SERS probe for the detection of Hg^{2+} [127], as illustrated in Fig. 6A. 4-mercaptopyridine (4-MPY) conjugated Ag NPs (Ag NPs-MPY) aggregated in $\text{Na}_2\text{HPO}_4\text{--NaH}_2\text{PO}_4$ buffer solution (pH=6.6) containing PEG10000 and NaCl, showing a strong SERS peak at 1097 cm^{-1} ; however, the presence of Hg^{2+} induced the peak intensity decrease by forming the stable complex of $[\text{Hg}(\text{MPY})_2]^{2+}$. Based on this sensing strategy, the SERS intensity was linear to Hg^{2+} concentration in the range of 50–3000 nmol/L, and satisfactory recoveries were obtained for the determination of Hg^{2+} in three river water samples. Chen and coworkers proposed another SERS nanoprobe based on the aggregation of Ag NPs [128]. Sodium 2-mercaptoethanesulfonate (mesna) modified Ag NPs aggregated in high salt solution, accompany with a strong SERS peak. Because the covalent bond of Hg-S was stronger than that of Ag-S, the adsorption of mesna on the surfaces of Ag NPs was suppressed. Thus, the decrease of Raman peak at 795 cm^{-1} was linear in the range of

0.01–2 $\mu\text{mol L}^{-1}$ with a detection limit of 0.0024 $\mu\text{mol L}^{-1}$. Moreover, the detection of Hg^{2+} in 6-benzylaminopurine-Ag NPs and methimazole-Ag NPs systems were also realized by this principle [126, 131].

Fig. 6

The second kind of nanoparticle aggregation based SERS nanosensor is designed based on oxidation-reduction reactions. In 2014, Chen *et al.* developed a simple and sensitive SERS nanosensor based on 4-MPY functionalized Ag NPs (4-MPY-Ag NPs) with the help of spermine [129]. As seen from Fig. 6B, the addition of spermine could induce the remarkable aggregation of 4-MPY-Ag NPs through Ag–N bond, which significantly enhanced Raman intensity of the reporter molecule 4-MPY. When Hg^{2+} was introduced, the obvious decrease of Raman intensity was obtained because the formed of the Hg–Ag alloy blocked the adsorption of 4-MPY and spermine. The proposed method showed high sensitivity and selectivity toward Hg^{2+} , and has been successfully used to detect Hg^{2+} in a real water sample. Kang *et al.* used the selective chemical reaction between Hg^{2+} and terminal ethynyl groups to realize the SERS determination of Hg^{2+} [129]. The formation of $-\text{C}\equiv\text{C}-\text{Hg}-\text{C}\equiv\text{C}-$ linkage led to the aggregation of 1,4-diethynylbenzene (DEB) modified Ag NPs, generating numerous hot spots which cause a substantial increase in the intensity of the SERS signal at 2,146 cm^{-1} . Under optimal conditions, the rationed signal intensity was related to concentration of Hg^{2+} in the range from 1.1 to 61.2 nM, with a detection limit at 0.8 nM. And the proposed method also displayed excellent selectivity over other metal ions and was successfully applied to the determination of Hg^{2+} in spiked river water.

1 T-Hg²⁺-T coordination chemistry is the third principle for the construction of
 2 nanoparticle aggregation based SERS nanosensors for Hg²⁺ detection. This kind of
 3 Hg²⁺ SERS nanosensors could be divided into types according to the modification of
 4 DNA on the surfaces of nanomaterials or not. In 2013, Ma *et al.* developed a SERS
 5 sensor for Hg²⁺ detection based on the self-assembly of nanostar dimer [137]. As
 6 depicted in Fig. 6C, two thiolated DNA oligonucleotides were modified on the
 7 surfaces of gold nanostars (Au NS) which could protect Au NS from aggregation.
 8 When adding Hg²⁺, Hg²⁺-mediated T-Hg²⁺-T coordination chemistry would induce
 9 the aggregation of Au NS, resulting in the increase of SERS intensity due to the
 10 enormous enhancement of the electromagnetic field by the dimer structures. This
 11 method provided a linear range from 0.002 to 1 ng/mL and a detection limit of 0.8
 12 pg/mL. Another typical example of “turn-on” SERS probe for the determination of
 13 Hg²⁺ and Ag⁺ was reported by Liu and coworkers based on the
 14 oligonucleotide-functionalized magnetic silica sphere (MSS)@Au NPs [140]. As
 15 schematically shown in Fig. 6D, the mismatched T-Hg²⁺-T and C-Ag⁺-C bridges
 16 employed in this system exhibited excellent responses to Hg²⁺ and Ag⁺. And Hg²⁺ and
 17 Ag⁺ could be effectively removed by an external magnetic field or through
 18 spontaneous precipitation. Additionally, the recycling of the MSS@Au NPs can reach
 19 more than 80% with the help of cysteine. Wang *et al.* reported a label-free and
 20 “turn-on” SERS probe to detect Hg²⁺ by using the aggregation of Ag NPs [141]. As
 21 schematically shown in Figure Fig. 6E, 5'-TAMRA-modified aptamer
 22 (5'-TAMRA-TTCTTTCTTCCCTTGTTTGTT-3') could bind with Ag NPs through

1 Ag–N bond to enhance the stability of Ag NPs, displaying mild aggregation in the
 2 presence of spermine with a weak SERS signal; on the contrary, the conformation of
 3 aptamer turned into folded structure in the presence of Hg^{2+} , reducing its capacity to
 4 inhibit Ag NPs from aggregation. The sensing system could quantify Hg^{2+} with a
 5 detection limit of 5 nmol/L.

6 **4.2 Hg^{2+} induced signal alteration on SERS active and support-assisted** 7 **nanomaterials**

8 Compared with the direct aggregation of nanoparticle based SERS detection toward
 9 Hg^{2+} , the reported Hg^{2+} -mediated SERS sensors using support-assisted
 10 nanomaterials are relatively rare. Support-assisted nanomaterials are composed of
 11 high-density and reproducible hot spot nanomaterials and support materials.
 12 Commonly, the widely used support materials include silica, polystyrene, and polymer
 13 beads, which are used for depositing noble metal nanoparticles. For instance, Zheng
 14 and coworkers designed a SERS detection platform which was consisted of a gold
 15 nanohole array and a SERS probe (a gold nanostar@Raman-reporter@silica sandwich
 16 structure) [142]. As schematically shown in Fig. 7A, the Au nanostar@MGITC@ SiO_2
 17 nanoparticles and the Au nanohole array were modified with the ssDNA of
 18 5'- NH_2 -(CH_2)₆-GTCTTTCTG-3' and 5'- NH_2 -(CH_2)₆-CAGTTTGAC-3', respectively.
 19 When adding Hg^{2+} , the formation of the T- Hg^{2+} -T base pairs induced the aggregation
 20 of nanoparticles. The strong plasmonic coupling between the Au nanostar and the Au
 21 nanohole array resulted in a large enhancement of the electromagnetic field, leading to
 22 amplification of the SERS signal. The SERS sensor had been successfully used to

1 detect Hg^{2+} in human saliva. Su *et al.* developed a SERS chip for the detection of
 2 Hg^{2+} with high sensitivity [143]. As depicted in Fig. 7B, the organic ligand
 3 4,4'-Dipyridyl (Dpy) could induce the aggregation of Au@Ag NPs and generate
 4 strong Raman hot spots and SERS readouts. On the contrary, the presence of Hg^{2+}
 5 could inhibit the aggregation of Au@Ag NPs by the coordination with Dpy, leading to
 6 the decrease of Raman intensity. Based on these findings, a SERS chip was fabricated
 7 by the assembly of Au@Ag NPs on a piece of silicon wafer and the further modified
 8 with Dpy. The exchange of Dpy from the chip into the aqueous Hg^{2+} droplet resulted
 9 in the quenching of Raman signals of Dpy. The test using the SERS chip only needed
 10 a droplet of 20 μL sample and could accomplish the whole detection within ~ 4 min.
 11 The SERS chip was also applied to the quantification of Hg^{2+} in milk, juice, and lake
 12 water. Guerrini *et al.* used Au NPs anchored polystyrene microparticles as SERS
 13 active substrates to realize the determination of Hg^{2+} and CH_3Hg^+ in aqueous solution
 14 [144]. As illustrated in Fig. 7C, 4-MPY could strongly bind gold via its mercapto
 15 group, and coordinate with mercuric species via the nitrogen of the pyridine moiety.
 16 Due to the different complexation of the inorganic and organic mercury with 4-MPY,
 17 it could distinguish between inorganic and organic mercury at trace levels by the
 18 unique and characteristic changes of SERS peaks. Kandjani *et al.* reported a sensitive
 19 SERS sensor for the detection of Hg^{2+} based on Si substrates supported ZnO/Ag
 20 nanoarrays [145], as shown in Fig. 7D. This ZnO/Ag nanoarrays based SERS sensor
 21 showed high sensitivity and selectivity toward Hg^{2+} , and could remove Hg^{2+} with the
 22 added multifunctionality of photocatalytic activity. More attractively, the ZnO/Ag

1 nanoarrays could be regenerated and reused over many cycles.

2 **Fig. 7**

3 **5 Conclusions and outlook**

4 In this review, we centered on discussing the reported nanomaterial-based optical
5 sensors for the detection of Hg^{2+} . Three kinds of optical nanosensors including
6 colorimetric assay, fluorometric analysis and SERS detection have been summarized
7 for their different detection mechanisms. The nanosensors show high sensitivity and
8 selectivity, simplicity, rapidity, and cost-effectiveness toward Hg^{2+} , and their
9 application potentials in real samples have also been explored.

10 Despite of many distinct advantages for Hg^{2+} detection, the nanomaterial-based
11 optical sensors still face great development challenges and opportunities, for example
12 as follows. The highly active characteristics and weak self-stability of nanomaterials
13 often lead to the limited suitability to complex real systems and thereby the optical
14 nanosensors seem more proof-of-concept especially for the aggregation-based sensors.
15 In order to satisfy the detection demands of Hg^{2+} in complicated matrices such as
16 seawater, wastewater, food additives and biological samples, the researchers should
17 pay more attentions on synthesizing new stable nanomaterials and designing novel
18 modification strategies to improve the functionalizing and applicability in complex
19 practical samples. Selectivity is another vital parameter for a sensor. Therefore,
20 appropriately screening and reasonably utilizing available ligands, and furthermore,
21 smartly devising and preparing new ligands with high specificity toward Hg^{2+} are
22 effective ways to enhance the detection selectivity. Moreover, rapid on-site sensing of
23 Hg^{2+} is always the pursuing goal. Fusion and integration of the versatile optical

nanotechnologies with test strips, microfluidic/paper chips, membrane and other technologies/strategies, will bring about promising perspectives for portable devices with commercial and industrial applications to monitoring/detecting Hg^{2+} ions.

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22 **Fig. 1** (A) Schematic colorimetric sensing mechanism of Hg^{2+} with
23 N-1-(2-Mercaptoethyl)thymine modified Au NPs. Reproduced with permission from

ref. 52. Copyright © 2011 The Royal Society of Chemistry. (B) Scheme mechanism of mercury(II)-controlled approach using quaternary ammonium group-terminated thiols modified Au NPs. Reproduced with permission from ref. 48. Copyright © 2010 American Chemical Society. (C) Schematic mechanism of sensing Hg^{2+} based on the Hg^{2+} -mediated the disassembly of Au NRs. Reproduced with permission from ref. 71. Copyright © 2012 Springer International Publishing AG, Part of Springer Science+Business Media. (D) Schematic representation of deoxythymidine triphosphates (dTTPs)-functionalized Au NPs for the detection of Hg^{2+} . Reproduced with permission from ref. 54. Copyright © 2011 The Royal Society of Chemistry. (E) Schematic sensing mechanism of detecting Hg^{2+} based on DNA-functionalized Au NPs. Reproduced with permission from ref. 53. Copyright © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Fig. 2 (A) Schematic illustration of Hg^{2+} -mediated anti-aggregation of Ag NPs. Reproduced with permission from ref. 67. Copyright © 2014 Elsevier B.V. (B) Scheme mechanism of Au NPs based colorimetric detection of Hg species. Reproduced with permission from ref. 72. Copyright © 2014 American Chemical Society. (C) Schematic illustration of Tween 20-Au NPs for sensing Hg^{2+} and Ag^+ . Reproduced with permission from ref. 73. Copyright © 2010 American Chemical Society. (D) Schematic representation of colorimetric detection of Hg^{2+} and Ag^+ based on redox reaction modulated surface chemistry of Au NPs. Reproduced with permission from ref. 62. Copyright © 2011 American Chemical Society. (E) Schematic mechanism of sensing Hg^{2+} based on anti-aggregation of Au NPs. Reproduced with permission from ref. 57. Copyright © 2012 American Chemical Society. (F) Schematic mechanism of colorimetric assay: (a) the interaction of the UMDP with two target ions, and (b) label-free colorimetric detection of Hg^{2+} and Ag^+ . Reproduced with permission from ref. 60. Copyright © 2012 American Chemical Society.

Fig. 3 (A) Schematic sensing mechanism of the formation of the amalgamation between Hg and Au NRs (a), and TEM and EDX analysis (b) of Au NRs in the absence (I) and the presence of Hg^{2+} with the concentration of 1.25×10^{-5} M (II) and 1.57×10^{-4} M (III). Reproduced with permission from ref. 74. Copyright © 2006 American Chemical Society. (B) Schematic representation of Hg^{2+} -modulated morphology transition of $\text{C}_{12}\text{H}_{25}\text{SH}$ -functionalized Ag NPRs in the presence of I^- . Reproduced with permission from ref. 77. Copyright © 2013 American Chemical Society. (C) Schematic mechanism of Hg^{2+} catalyzed $\text{HAuCl}_4/\text{NH}_2\text{OH}$ reaction in the absence (a) and presence (b) of Hg^{2+} . Reproduced with permission from ref. 75. Copyright © 2010 Elsevier B.V.

Fig. 4 Schematic sensing mechanism for Hg^{2+} detection based on metal-induced aggregation of MPA coated Mn doped ZnSe/ZnS QDs. Reproduced with permission from ref. 101. Copyright © 2016 Macmillan Publishers Limited.

Fig. 5 (A) Schematic sensing mechanism for Hg^{2+} detection based on $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ upconversion nanoparticle (UCNP)/CdTe QD composite. Reproduced with permission from ref. 106. Copyright © 2015 The Royal Society of Chemistry. (B) The illustration of the principle (a) of the QD/DNA/Au NP sensor for Hg^{2+} detection, fluorescence emission spectra (b) and photo image (c) under 365 nm laser excitation of the QD/DNA/Au NP solution in the absence and presence of $1\ \mu\text{M}$ Hg^{2+} . Reproduced with permission from ref. 99. Copyright © 2011 American Chemical Society.

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Fig. 6 (A) Schematic mechanism of Hg^{2+} detection based on the aggregation of Ag NPs. Reproduced with permission from ref. 127. Copyright © 2012 Elsevier B.V. (B) Schematic sensing mechanism of Hg^{2+} mediated SERS sensor. Reproduced with permission from ref. 129. Copyright © 2014 The Royal Society of Chemistry. (C) Schematic representation of Hg^{2+} SERS detection based on the self-assembly of Au NS dimers. Reproduced with permission from ref. 137. Copyright © 2013 The Royal Society of Chemistry. (D) Schematic illustration of the SERS $\text{Hg}^{2+}/\text{Ag}^+$ detection using DNA-Au NPs and DNA-MSS@Au NPs. Reproduced with permission from ref. 140. Copyright © 2014 American Chemical Society. (E) Schematic of the SERS sensing principle for Hg^{2+} based on label-free Ag NPs [141].

Fig. 7 (A) The prepared procedure (a-f) of gold nanohole array, (h) SEM image of a gold nanohole array, (i) experimentally measured (black curve) and FDTD simulated (blue curve) transmission of the Au nanohole array and (j) the operating principle of the SERS sensor. Reproduced with permission from ref. 142. Copyright © 2015 The Royal Society of Chemistry. (B) Schematic illustration of (a) the interaction between Au@Ag NPs and 4,4'-dipyridyl (Dpy) in the absence and the presence of Hg^{2+} and the corresponding SERS responses, and (b) direct detection of Hg^{2+} with the SERS chip fabricated by the assembly of Au@Ag NPs on a silicon wafer. Reproduced with permission from ref. 143. Copyright © 2013 American Chemical Society. (C) (a) SERS spectra of MPY on PS@Au beads upon the addition of CH_3Hg^+ , a mixture of Hg^{2+} and CH_3Hg^+ and Hg^{2+} , and (b) schematic outlines of the coordination processes [144]; (D) Detailed (a) synthesis and (b) sensing, removal and regeneration processes of ZnO/Ag nanoarrays. Reproduced with permission from ref. 145. Copyright © 2015 American Chemical Society.

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Table 1 Key characteristics of colorimetric nanosensors for Hg^{2+} analysis based on the aggregation of nanomaterials

Nanomaterial	Sensing strategy	Linear range	Detection limit	Analytical application	Ref.
Au NPs	Hg^{2+} induced aggregation of 3-mercaptopropionic acid-functionalized Au NPs in the presence of 2,6-pyridinedicarboxylic acid.	250–500 nM	100 nM	—	[46]
Au NPs	Hg^{2+} induced aggregation of 3-mercaptopropionate acid and adenosine monophosphate modified Au NPs in a high-salinity solution.	0.5–3.5 μM	500 nM	—	[47]
Au NPs	The addition of Hg^{2+} dissociated the quaternary ammonium group-terminated thiols from the surfaces of Au NPs, leading to the aggregation of Au NPs.	0–600 nM	30 nM	Drinking water	[48]
Au NPs	The addition of Hg^{2+} induced the aggregation of specific DNA-functionalized Au NPs based on the folding of mercury-specific DNA strand through the T- Hg^{2+} -T coordination.	0.1–10 μM	60 nM	Fish tissue samples	[49]
Au NPs	Hg^{2+} induced aggregation of papain-functionalized Au NPs.	—	200 nM	Lake water, tap water	[50]

Au NPs	The aggregation of Au NPs with bare surfaces were generated by the displacement of calixarene derivative from the surfaces of Au NPs due to its strong complexation ability to Hg^{2+} .	0.2–100 μM	40 ppb	Drinking water	[51]
Au NPs	The addition of Hg^{2+} led to the aggregation of N-1-(2-Mercaptoethyl)thymine modified Au NPs via forming a T- Hg^{2+} -T complex.	5–1000 nM	2.8 nM	Tap water	[52]
Au NPs	The colorimetric detection method relied on T- Hg^{2+} -T coordination chemistry and complementary DNA-Au NPs with deliberately designed T-T mismatches.	—	100 nM	—	[53]
Au NPs	The desorption of deoxythymidine triphosphates from the surfaces of Au NPs by Hg^{2+} induced aggregation of Au NPs.	0.2–6.0 μM	0.05 μM	Tap water, river water	[54]
Au NPs	The formation of DNA duplexes by T- Hg^{2+} -T coordination chemistry induced that Au NPs are less protected, resulting to the aggregation of Au NPs at the same salt concentration.	0–5 μM	0.5 μM	—	[55]
Au NPs	The formation of Au-Hg alloys induced the aggregation of Au NPs.	0–9.0 μM	35 nM	Drinking water	[56]
Au NPs	Anti-aggregation of Au NPs induced by the coordination	2–12 μM	2 nM	Tap water	[57]

	between thymine and Hg^{2+} .				
Au NPs	The addition of lysine led to the aggregation of Hg^{2+} -capped Au NPs.	1 nM–1 μM	2.9 nM	Tap water	[58]
Au NPs	A colorimetric logic gate based on Au NPs and the coordination interaction between melamine and Hg^{2+} .	50–250 nM	50 nM	Lake water	[59]
Au NPs	The presence of Hg^{2+} changed DNA probe into hairpin structure, which facilitated the salt induced Au NPs aggregation.	0.75–1.5 μM	0.25 μM	Lake water, tap water	[60]
Au NPs	Anti-aggregation of Au NPs induced by the binding between 4-mercaptophenylboronic acid and Hg^{2+} .	0.01–5 μM	8 nM	Lake water	[61]
Au NPs	Hg^{2+} was reduced by ascorbic acid to form Hg–Au alloy coating on the surfaces of Au NPs, which blocked the assembly of mercapto ligand and made Au NPs keeping monodisperse after addition of N-acetyl-L-cysteine.	0.5–10 μM	5 nM	Tap water, drinking water	[62]
Au NPs	The anti-aggregation of Au NPs from the deactivation of 4,4'-dipyridyl by Hg^{2+} .	40 nM–1.1 μM	15 nM	Tap water, spring water	[63]
Ag NPs	The addition of Hg^{2+} caused the conformation change of mercury-specific oligonucleotides from random coil	25–500 nM	17 nM	—	[64]

	structure to hairpin structure, accompany with the salt-induced aggregation of unmodified Ag NPs.				
Ag NPs	The polydopamine adsorption with Hg^{2+} could induce the aggregation of Ag NPs.	0.5–5.0 μM	50 nM	Tap water	[65]
Ag NPs	Ag NPs mediated reduction of Hg^{2+} to Hg^0 in the presence of H_2O_2 , leading to the aggregation and colorimetric response of Ag NPs.	0.02–900 nM	—	Drinking water	[66]
Ag NPs	Hg^{2+} -inhibited aggregation of Ag NPs.	0–333 nM	4 nM	Spring water.	[67]
Au NRs	The addition of Hg^{2+} caused the aggregation of L-cysteine functionalized Au NRs.	3–6 ppb	3 ppt	—	[68]
Au NRs	The deprotonated amine group of L-arginine on the Au NRs bound with Hg^{2+} leading to the side-by-side assembly of Au NRs.	1–20 μM , 20–600 μM	5 nM	—	[69]
Au NRs	The presence of Hg^{2+} induced the aggregation of N-alkylaminopyrazole functionalized Au NRs.	0–6 ppb	3 ppt	—	[70]
Au NRs	The competitive binding between Hg^{2+} and cysteine induced the disassembly of self-assembled-Au NRs.	0.5–250 μM	0.06 μM	Lake water, tap water	[71]

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Table 2 Key characteristics of fluorescent nanosensors for Hg^{2+} analysis

Nanomaterial	Sensing strategy	Linear range	Detection limit	Analytical application	Ref.
Ag NCs	Hg^{2+} -induced the changes of poly(acrylic acid)-templated the Ag NCs states.	0–20 μM	2 nM	River water, tap water, mineral water	[85]
Au NCs	The addition of Hg^{2+} caused the aggregation-induced fluorescence quenching of glutathione-capped Ag NCs.	0.1 nM–10 μM	0.1 nM	drinking water	[86]
Au NCs	Hg^{2+} could bind with the Au^+ from bovine serum albumin stabilized Au NCs.	25 nM–5 μM	8 nM	Tap water, electroplating wastewater	[87]
Ag NCs	The partial Ag oxidation and the formation of Ag-Hg amalgam caused the fluorescence quenching of Ag NCs prepared by polyinosinic acid (PI) or polycytidylic acid (PC).	PI: 0.05–1.0 μM PC: 0.5–10 μM	PI: 3.0 nM PC: 9.0 nM	Lake water	[88]
Au NCs	The forming of T- Hg^{2+} -T duplexes led to the quenching of fluorescence.	0.1–100 μM	0.083 μM	Human urine, lake water	[89]
Ag NCs	Hg^{2+} -mediated interparticle aggregation quenched the	0–1 μM	5 nM	Tap water, spring	[90]

	fluorescence of DNA–Ag NCs.			water	
Ag NCs	Hg ²⁺ -mediated label-free hairpin DNA-scaffolded Ag NCs accompanying exonuclease III-assisted target recycling amplification.	0.1–10 nM	24 pM	Tap water, seawater, sewage water	[91]
AuAgS/Ag ₂ S NCs	Hg ²⁺ closed to the AuAgS/Ag ₂ S NCs could form HgS resulting to the quenching of fluorescent nanoclusters.	—	10 ⁻¹³ M	Fish samples	[92]
Au-Ag NCs	The fluorescence quenching of Au-AgNCs was resulted from the interactions between Hg ²⁺ ions and Au of Au-AgNCs by metallophilic bonding of 5d ¹⁰ centers.	0.20–2500 nM	0.10 nM	Blood samples	[93]
Pt-Au NCs	The d ¹⁰ -d ¹⁰ metallophilic interaction between Hg ²⁺ and Au ⁺ induced the quenching of fluorescent BSA-Pt-Au NCs.	0.5 nM–22 μM	0.3 nM	Urine, serum	[94]
CdTe QDs	The decrease of dBSA-coated CdTe QDs emission was due to both electron transfer and ion-binding.	0.012–1.5 μM	4.0 nM	Pond water, fountain water	[95]
CdS QDs	Hg ²⁺ could bind carboxyl and carbonyl groups on the surfaces of mercaptoacetic acid capped CdS QDs.	5–400 nM	4.2 nM	—	[96]
CdSe QDs	The formation of a stable complex (QDs–I [–] –Hg ²⁺) could induce effective electron transfer from the QDs to the Hg ²⁺ , which was responsible for the	0–35 μM	0.19 μM	—	[97]

	fluorescence quenching of QDs.				
CdS QDs	The binding between Hg^{2+} and L-cysteine induced the aggregation of L-cysteine -capped CdS QDs.	1.0–9.0 nM	1.0 nM	—	[98]
CdSe/ZnS QDs, Au NPs	The formation of T- Hg^{2+} -T complexes brought the nanometal surface energy transfer (NSET) from the QDs to the Au NPs.	2–60 nM	2 nM	River water	[99]
CdTe QDs	The strong affinity of Hg^{2+} to N atom, the formation of alloyed $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ and the band alignment induced the quenching of the fluorescence of cysteamine-CdTe QDs.	0.08–3.33 μM	0.07 μM	—	[100]
Mn-doped ZnSe/ZnS QDs	The presence of Hg^{2+} could separate mercaptopropionic acid (MPA) from MPA coated Mn doped ZnSe/ZnS QDs, resulting the aggregation and fluorescence quenching of QDs.	0–1.5 nM	0.1 nM	Drinking water	[101]
Mn-doped ZnS QDs	The bind between Hg^{2+} and thymine bases induced electron transfer quenching of the QDs.	50–800 nM	1.5 nM	Tap water, river water	[102]
N-doped GQDs	The effective quenching effect of Hg^{2+} via nonradiative electron transfer.	0.04–6 μM	8.6 nM	River water	[103]
GQDs	Hg^{2+} binded with carboxylate groups on the surface of GQDs, inducing aggregation of GQDs aggregated to	0.8–9 μM	0.1 μM	—	[104]

	some extent and the quenching of fluorescence.				
O and S co-doped GNCQDs	The strong interactions between Hg^{2+} and pyridine nitrogen in oxygen and sulfur co-doped graphitic carbon nitride quantum dots (OS-GNCQDs) generated energy transfer from OS-GNCQDs to Hg^{2+} .	0.001–20.0 μM	0.37 nM	Cell imaging	[105]
CdTe QDs $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ UCNPs	The specific interaction between Hg^{2+} and carboxyl on the surfaces of QDs quenching the fluorescence of QDs through the FRET from $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ UCNPs to CdTe QDs.	20–800 nM	15 nM	Human serum	[106]
CDs, $\text{CdSe}@\text{ZnS}$ QDs	Hg^{2+} could dissociate carboxymethyldithiocarbamate (GDTC) from the surfaces of GDTC-QDs, which could selectively quenched the fluorescence of GDTC-QDs. And the fluorescence of the CDs remained constant, resulting in a distinguishable ratiometric fluorescence detection.	0.2–2 μM	0.1 μM	Tap water, lake water	[107]
CDs	The binding between the Hg^{2+} and carboxylic groups led to the decreasing fluorescence intensity.	CDs-1: 1–12 μM CDs-2: 1–15 μM	CDs-1: 226 nM CDs-2: 845 nM	River water, mineral water	[108]
N-doped CDs	The fluorescence quenching attributed to two factors:	0–25 μM	0.23 μM	Tap water, lake	[109]

	the nonradiative electron-transfer from the excited states to the d orbital of Hg^{2+} , and Hg^{2+} -induced conversion of the functional group ($-\text{CONH}-$) from spirolactam structure to an opened-ring amide.			water	
$\text{Eu}^{3+}/\text{CDs@MOF-253}$	Hg^{2+} adsorbed onto the surface of CDs as a surface modifier and coordinated with the organic functional groups, changing the surface traps or electron-hole recombination annihilation via electron or energy transfer processes and quenching the fluorescence of CDs.	0.065–150 μM	13 ppb	River water, fountain water, tap water	[110]
CdTe QDs	The strong affinity of Hg^{2+} with carboxyl groups led to an electron transfer between the CdTe QDs and Hg^{2+} .	8.0–800 ng L^{-1}	0.66 ng L^{-1}	River water	[111]
Ce^{3+} and Tb^{3+} -doped SrF_2 nanocrystals	The strong interaction between Hg^{2+} and thiol groups presented in GSH quenched the fluorescence.	1–10 μM	20 μM	Lake water, tap water, mineral water	[112]
Self-assembled fluorescent nanostructures of cephalixin	The binding of Hg^{2+} and sulfur moiety of cephalixin molecule induced the quenching.	—	—	—	[113]

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Table 3 Key characteristics of SERS nanosensors for Hg^{2+} analysis

Nanomaterial	Sensing strategy	Linear range	Detection limit	Analytical application	Ref.
Ag NPs	The stable complex of $[\text{Hg}(\text{MPY})_2]^{2+}$ induced the decrease of Raman intensity.	50–3000 nM	30 nM	River water	[127]
Ag NPs	The covalent bond of Hg-S was stronger than that of Ag-S, suppressing the adsorption of mesna on the surfaces of Ag NPs.	0.01–2 μM	0.0024 μM	Lake water, groundwater	[128]
Ag NPs	The formation of the Hg–Ag alloy blocked the adsorption of 4-MPY and spermine.	1–100 nM	0.34 nM	Tap water	[129]
Ag NPs	Hg^{2+} reduced the adsorption of 6-BA molecules on the surfaces of Ag NPs, causing the decrease of SERS signal of 6-BA.	5–200 $\mu\text{g/L}$	0.2 $\mu\text{g/L}$	Drinking mineral water	[130]
Ag NPs	The formed Hg^{2+} –Ag particles catalyzed a redox reaction between o-phenyldiamine and dissolved oxygen to form 2,3-diaminephenazine, which possessed a strong SERS signal by the adherence to Ag NPs.	1 nM–10 mM	1.0 nM	Tap water	[131]
Au NPs	A competitive immunoassay using	10^{-3} –100	0.45pg/mL	Lake water, river	[132]

	immunochromatographic test.	ng/mL		water, tap water, serum, urine	
Ag NPs	The selective chemical reaction between Hg^{2+} and the terminal ethynyl groups formed a $-\text{C} \equiv \text{C}-\text{Hg}-\text{C} \equiv \text{C}-$ linkage which triggers the aggregation of Ag NPs.	1.1–61.2 nM	0.8 nM	River water	[133]
Au NPs	Hg^{2+} induced DNA modified Au NPs assembled into chains which were displayed remarkable SERS signal.	0.001–0.5 ng/mL	0.45 pg/mL	Drinking water	[134]
Ag NPs	In the presence of Hg^{2+} , methimazole molecules released from the surface of Ag NPs due to the reaction of methimazole and Hg^{2+} , which caused the decreases of SERS signal.	0.50–150 $\mu\text{g/L}$	0.10 $\mu\text{g/L}$	Tap water, lake water, reservoir water, river water	[135]
Au NRs	The $\text{T}-\text{Hg}^{2+}-\text{T}$ coordination chemistry induced the assembly of side-by-side Au NR oligomers.	5–5000 pM	4.3 pM	Tap water	[136]
Au NS	Hg^{2+} -mediated $\text{T}-\text{Hg}^{2+}-\text{T}$ coordination chemistry induced the aggregation of Au NS, resulting in the increase of SERS intensity.	0.002–1 ng/mL	0.8 pg/mL	—	[137]
Ag NRs	The galvanic replacement reaction between Ag NRs and Hg^{2+} induced the decrease of Raman intensity.	1.25–125 nM	0.2 nM	Cosmetic sample	[138]
Ag_2Te NPs	The interaction of Ag_2Te NPs with Hg^{2+} led to the formation of HgTe NPs, leading to decreases in the	10–150 nM	3 nM	Pond water	[139]

	SERS signal of R6G.				
Magnetic silica sphere @Au NPs, Au NPs	The mismatched T-Hg ²⁺ -T made the aggregation of oligonucleotide-functionalized magnetic silica sphere @Au NPs and DNA-Au NPs.	0.1–1000 nM	0.1 nM	—	[140]
Ag NPs	The conformation of aptamer turned into folded structure in the presence of Hg ²⁺ , reducing its capacity to inhibit Ag NPs from aggregation.	—	5 nM	—	[141]
Gold nanohole array, Au nanostar@MGITC@SiO ₂ nanoparticles	T-Hg ²⁺ -T base pairs induced the aggregation of nanoparticles, and the strong plasmonic coupling between Au nanostar and the Au nanohole array resulted in the amplification of the SERS signal.	5 pM–100 nM	2.3 pM	Saliva	[142]
Au@Ag NPs assembled silicon wafer	The exchange of Dpy from the chip into the aqueous Hg ²⁺ droplet resulted in the quenching of Raman signals of Dpy.	1×10 ⁻⁴ –0.1 nM	1×10 ⁻⁴ nM	Milk, juice, lake water	[143]
Au NPs anchored polystyrene microparticles	The different complexation of the inorganic and organic mercury with 4-MPY.	Hg ²⁺ : — CH ₃ Hg ⁺ : 0–15 ppb	Hg ²⁺ : 50 ppt CH ₃ Hg ⁺ : 1.5 ppb	—	[144]
ZnO/Ag nanoarrays	Photocatalytic reduction of Hg ²⁺ to elemental mercury.	—	0.45 ppb	—	[145]