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Recent developments on nanomaterials-based optical sensors for Hg^{2+} detection

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Mercuric ion (Hg^{2+}), released from both natural and industrial sources, has severe adverse effects on human health and the environment even at very low concentrations. It is very important to develop a rapid and economical method for the detection of Hg^{2+} with high sensitivity and selectivity. Nanomaterials with unique size and shape-dependent optical properties are attractive sensing materials. The application of nanomaterials to design optical sensors for Hg^{2+} provides a powerful method for the trace detection of Hg^{2+} in the environment, because these optical sensors are simple, rapidly responsive, cost-effective and highly sensitive. This review summarizes the recent advances on the development of optical assays for Hg^{2+} in aqueous solution by using functionalized nanomaterials (including noble metal nanoparticles, fluorescent metal nanoclusters, semiconductor quantum dots and carbon nanodots). Detection strategies based on the Hg^{2+}-induced changes in spectral absorbance, fluorescence intensity and surface-enhanced Raman scattering signals were described. And the design principles for each optical assay were presented. In addition, the future challenge and the prospect of the development of nanomaterial optical sensors for Hg^{2+} detection were also discussed.

INTRODUCTION

Much attention has been paid to the contamination of the environment with toxic heavy metal ions for decades [1]. Among them, mercury is a well-known dangerous pollutant which can exist in metallic, inorganic and organic forms. As one of the most stable and wide-spread form of inorganic mercury, water-soluble mercuric ion (Hg^{2+}), released from both natural sources (volcanic and oceanic emissions) and industrial sources (chemical manufacturing, fossil fuel combustion, as well as solid waste incineration), can cause severe damage to human health and the environment even at low concentrations [2]. Bacteria living in aquatic sediments can convert Hg^{2+} to methylmercury, a potent neurotoxin that can accumulate in the human body through food chain and cause permanent damage to the brain with serious symptoms such as deafness, vision loss and motor and cognitive disorders [3]. The USA Environmental Protection Agency (EPA) establishes the maximum contaminant level for Hg^{2+} in drinking water at 2 $\mu g\ L^{-1}$ (10 nM). Therefore, the rapid, economical, sensitive and selective detection of trace Hg^{2+} in the environment is urgently needed.

The current analytical methods for the detection of Hg^{2+} include atomic absorption spectroscopy [4], cold vapor atomic fluorescence spectrometry [5], inductively coupled plasma mass spectrometry [6], electrochemical methods [7], gas chromatography [8] and high performance liquid chromatography [9]. Although many of these methods can provide low detection limits, they usually require expensive equipment or complicated sample preparation processes. Furthermore, they are time-consuming and not suitable for *in-situ* analysis.

As alternative methods, optical sensors have been demonstrated to be a quick and simple approach. In particular, nanomaterials with unique optical properties provide opportunities for developing new generation of optical sensors with high sensitivity and selectivity. The optical properties of nanomaterials vary with their surrounding chemical environment, which provides a foundation for the pollutant sensing [10]. The application of nanomaterials to design optical sensors for Hg^{2+} is nowadays one of the most active research fields due to their cost-effectiveness, simplicity and rapidity. These optical sensors can be classified into colorimetric, fluorescence and surface-enhanced Raman scattering (SERS) sensors, depending on the origin of the optical signals. By utilizing changes of the spectral absorbance, fluorescence intensity and SERS signals, the trace concentration of Hg^{2+} can be quantitatively detected. In the design of Hg^{2+} optical sensors, noble metal nanoparticles (NPs), fluorescent metal nanoclusters (NCs), semiconductor quantum dots (QDs) and carbon nanodots (CDs) are the commonly used optical sensing nanomaterials owing to their ease of synthesis and functionalization, high stability and biocompatibility.

Metal NPs with strong surface plasmon resonance (SPR) absorption properties can be applied in the design of colorimetric and SERS sensors [11]. The SPR absorption wave-

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length of metal NPs depends on their particle size, shape, composition, and aggregation state. It is tunable throughout the visible and near-infrared region of the spectrum. Colloidal solutions of metal NPs (Au NPs and Ag NPs) have different color in the visible region of the spectrum when they are dispersed compared with when they are aggregated. The color-change behavior depending on the aggregation state of metal NPs (Au NPs and Ag NPs) allows the visual detection of Hg^{2+} by the naked eyes [12]. The SPR excitation of metal NPs enhances local electromagnetic field which is responsible for the strong SERS signals [13]. Metal NPs-based SERS sensor for Hg^{2+} can reach high sensitivity. Apart from the use as colorimetric and SERS sensors, Au NPs with strong molar absorptivities are super quenchers for fluorophores, which allows them to be employed in the fluorescence detection of Hg^{2+} [14]. Metal NCs, QDs and CDs possess high fluorescence [15–17] and they can be used for the development of sensitive fluorescent sensors. Among them, QDs are the most commonly used fluorescent NPs [18]. Compared with traditional organic dyes, QDs have tunable narrow emission spectra, high quantum yields, long luminescence lifetime and negligible photo-bleaching. Both metal NCs and CDs are emerging as alternative to QDs due to their nontoxicity and good biocompatibility. It is noted that all of these nanomaterials-based optical sensors only need low-cost portable instruments and simple operation processes, enabling them perform in remote areas. In a word, nanomaterials-based optical sensors exhibit good advantages and potentials for detecting Hg^{2+}. Indeed, in the past 20 years we have witnessed a variety of nanomaterials-based sensors for mercury detection (as shown in Fig. 1), and the development of nanomaterials-based sensors for mercury has increased markedly in recent years.

Due to the simplicity and high sensitivity of nanomaterial optical sensors, there have been some reviews about the optical detection of different metal ions (such as Hg^{2+}, Pb^{2+}, Cu^{2+} and Cd^{2+}) in the aspects of colorimetric and fluorescent assays which were mainly based on Au NPs and QDs [19–25]. To date, there are only a few reviews for optical detection of Hg^{2+} by using fluorescent organic compounds as optical sensors [3,26,27]. And one of them discussed the application of nanomaterials (CdTe and InP nanocrystals, Au NPs and Au nanorods) as Hg^{2+} optical sensors [3]. Recently, one review paper about the application of Au NP-based colorimetric assays for Hg^{2+} was reported by Du *et al.* [28]. Besides, Botasini *et al.* [29] discussed the feasibility of nanotechnology-based sensors for Hg^{2+} analysis in real samples. They highlighted the needs of more realistic assays in future research for on-site analysis. In recent years, SERS has emerged as a powerful technique for applications in highly sensitive detection of Hg^{2+}. Besides, CDs as a fascinating class of recently discovered carbon nanomaterials are also used as environmentally-friendly fluorescence sensors for Hg^{2+}. It is necessary to comprehensively summarize the recent advances of optical detection of Hg^{2+} based on nanomaterials.

In this article, we systematically present a review of the development of nanomaterials-based optical sensors for the detection of Hg^{2+} in aqueous solution (Fig. 2). The review had three main sections according to the detection strategies based on Hg^{2+}-induced changes in absorption, fluorescence and SERS. Each section began with a short description of the commonly used nanomaterials and the design principle, then the applications of nanomaterials (including Au NPs, Ag NPs, Au NCs, Ag NCs, QDs and CDs) in optical sensing of Hg^{2+} were discussed. The future challenge and the prospect of the development of nanoma-

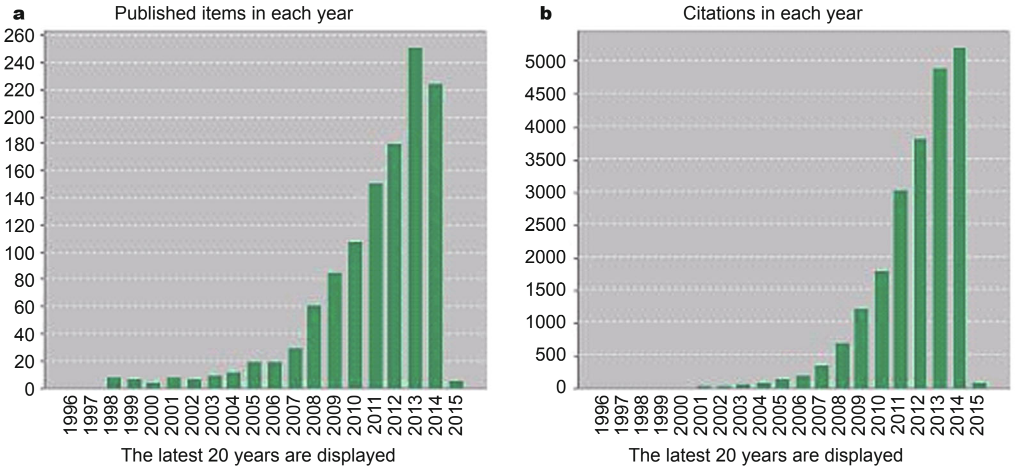

Figure 1 Evolution of the number of publications (a) and citations (b) concerning the use of nanomaterials as trace detection sensor for mercury analysis. Retrieved from the Web of Science.

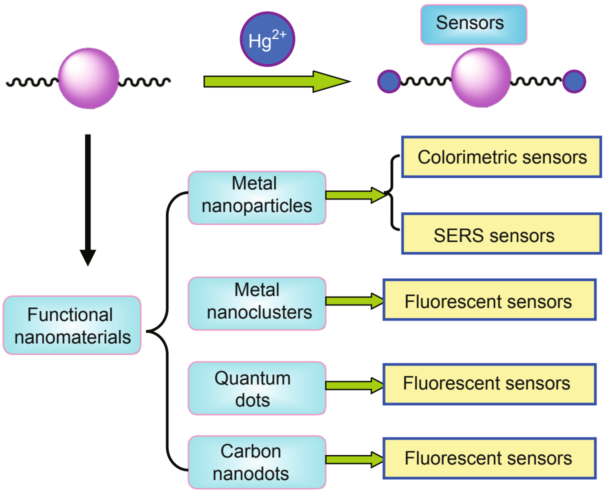

Figure 2 Applications of the functional nanomaterials as optical sensors for Hg^{2+}.

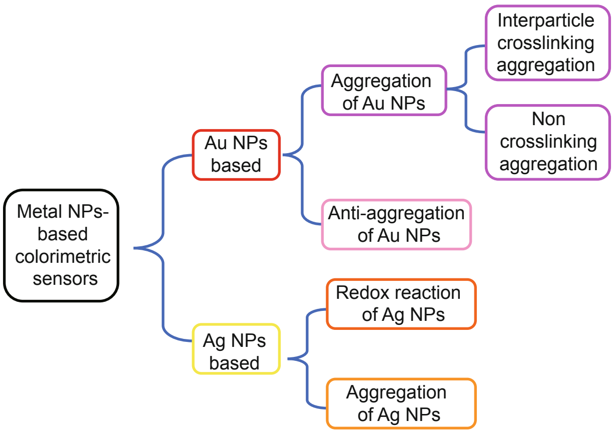

Figure 3 Sensing strategies of metal NPs as colorimetric sensors for Hg^{2+}.

terials-based optical sensors for Hg^{2+} were also presented.

COLORIMETRIC SENSORS

Colorimetric sensors are extremely attractive because the analytes can be easily read out by the naked eyes or concisely performed using UV/vis spectrometry free of expensive instruments. Functionalized metal NPs, including Au NPs and Ag NPs, are considered to be promising colorimetric reporters because they have high visible-region extinction coefficients (3–5 orders of magnitude higher than those of organic dyes) and possess strong SPR absorption properties [28]. Their unique tunable optical properties which are controlled by SPR depend on their size, shape, dielectric properties of the surrounding medium and interparticle distances. When the interparticle distances between the Au NPs or Ag NPs become less than the average particle diameter, a visual color change (red to blue for Au NPs and yellow to brown for Ag NPs from dispersion to aggregation state, respectively) as well as a red-shift of the SPR band would be observed. The color-change behavior depending on the interparticle distance of metal NPs provides the main basis for the development of colorimetric sensor. The main detection mechanism of Hg^{2+} colorimetric sensor is based on the fact that Hg^{2+} could induce aggregation/redispersion or the redox reaction of Au NPs/Ag NPs, which causes a color change in the solution (Fig. 3).

Au NPs-based colorimetric assays

In the Hg^{2+} colorimetric sensing system, Au NPs are the most commonly used metal NPs due to their high chemical stability and oxidation resistance. At present, two main sensing systems have usually been employed for the colorimetric detection of Hg^{2+}. One is based on Hg^{2+}-induced aggregation of Au NPs. Conversely, the other relies on Hg^{2+}-inhibited aggregation of Au NPs. The degree of aggregation is associated with Hg^{2+} concentration and the concentration of Hg^{2+} can be quantitatively detected according to the change in SPR band of Au NPs.

Between the two main sensing systems, the commonly used detection route is based on Hg^{2+}-induced aggregation of Au NPs. The complexation of Hg^{2+} with the capping ligands such as DNA and thiolates induces the aggregation of Au NPs with a red-to-blue color change and a red-shifted absorption band. In this aggregation-based assay, there exist two main kinds of sensing approaches. One is "interparticle crosslinking aggregation" by using the specific interactions between capping ligands and Hg^{2+}. The other is "non-crosslinking aggregation" based on the removal of Au NPs' surface bound stabilizers.

In the "interparticle crosslinking aggregation" approach, the classical method is based on DNA-functionalized Au NPs (DNA-Au NPs) through the formation of stable thymine-Hg^{2+}-thymine (T-Hg^{2+}-T) complex. For example, Mirkin's group [30] developed a complementary DNA-Au NP system with designed T-T mismatches for colorimetric detection of Hg^{2+}. The binding of the T-T mismatches with Hg^{2+} through T-Hg^{2+}-T complex formation induces a more thermally stable DNA duplex that has a higher melting temperature (T_m) compared with that in the absence of Hg^{2+}. The Hg^{2+} concentration was detected by monitoring the change in the solution color at the T_m of the DNA-Au NP aggregates. To avoid heating and develop a convenient system that can work at room temperature, Liu's group [31] improved this strategy through optimizing the DNA sequences and introducing an appropriate oligonucleotide linker. Another simple method based on the interparticle crosslinking aggregation mechanism is carried out by using Au NPs modified with thiolates such as 11-mercaptoundecanoic acid (11-MUA) [32], 3-mercaptopropionic acid (3-MPA) [33] and dithioerythritol (DTET) [34]. However, masking agents such as 2,6-pyridinedicarboxylic acid (PDCA) [35] and ethylene diamine tetraacetic acid (EDTA) [34] must be added to improve the selectivity in these colorimetric assays. Recently, (*N*-1-(2-mercaptoethyl)thymine)-modified Au NPs was designed as a colorimetric probe to detect Hg^{2+}. Based on the T-Hg^{2+}-T coordination chemistry, this colorimetric assay exhibited high selectivity for Hg^{2+} without any masking agent [36].

In the "non-crosslinking aggregation" approach, the typical method is also based on DNA-Au NPs [37–39]. Au NPs surface bound single-stranded DNA (ssDNA) with T-rich domains can protect the Au NPs from salt-induced aggregation. While in the presence of Hg^{2+}, the formation of T-Hg-T complex yields a hairpin structure, resulting in the abstraction of ssDNA from Au NPs surface and thus causing the aggregation of Au NPs at the same salt concentration (Fig. 4) [38]. Apart from the DNA-Au NPs based colorimetric assays, other colorimetric methods based on the non-crosslinking aggregation mechanism have also been reported. For example, Liu *et al.* [40] used Au NPs capped with quaternary ammonium group-terminated thiols (11-mercapto-undecyl)-trimethylammonium) to detect Hg^{2+}. The high affinity of thiolates toward Hg^{2+} induced the breakage of Au-S bonds on the Au NPs' surfaces, which caused dissociation of thiols from Au NPs surfaces. As a result, Au NPs aggregated with a color change from red to blue. Lin *et al.* [41] used Tween 20-capped Au NPs for sensing Hg^{2+} by the reduction of Hg^{2+} with citrate to form Hg-Au alloys, which dislodged Tween 20 from the surface of Au NPs and thus induced the Au NPs aggregation. Chen *et al.* [42] reported an Hg^{2+} colorimetric assay with a tunable dynamic range based on the coordination of Hg^{2+} to the Au NP-associated 3-nitro-1H-1,2,4-triazole (NTA). The NTA could protect Au NPs from the aggregation induced by 2-amino-2-hydroxymethyl-propane-1,3-diol (Tris). Upon the addition of Hg^{2+} and Tris, the NTA was removed from the Au NP surface via the formation of NTA-Hg^{2+} complex, resulting in Tris-induced aggregation of Au NPs. Similarly, Xu *et al.* [43] used the deoxythymidine triphosphates (dTTPs)-stabilized Au NPs for colorimetric detection of Hg^{2+}. The specific formation of dTTPs-Hg^{2+} complexes released the dTTPs from the Au NPs surface, thus inducing the aggregation of Au NPs (Fig. 5).

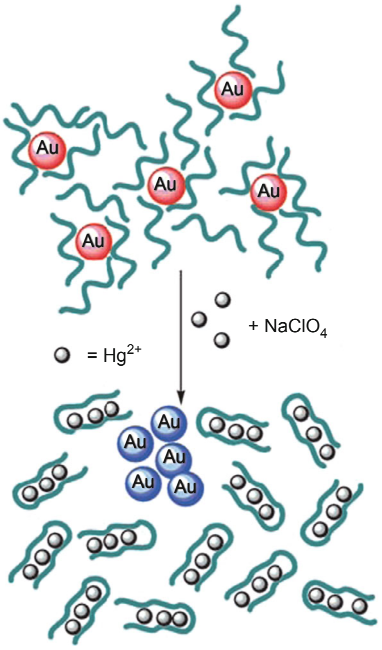

Figure 4 Hg^{2+}-ion-stimulated aggregation of Au NPs for the optical analysis of Hg^{2+} ions. Reproduced with permission from Ref. [38]. Copyright 2008, Wiley-VCH Verlag GmbH & Co. KGaA.

Compared with the commonly used Hg^{2+}-induced aggregation-based method, the Hg^{2+}-inhibited aggregation-based method can avoid the false positive results [44]. Besides, the latter method showed higher selectivity and seemed more eye-sensitive in low concentration of Hg^{2+} [45,46]. In this detection system, the addition of Hg^{2+} could inhibit the initially induced aggregation of Au NPs with a blue-to-red color change, through the competing combination with aggregation agents between Hg^{2+} and Au NPs. The concentration of Hg^{2+} could be easily detected by simply mixing the aggregation reagents and Au NPs without any complicated modifying step. In addition, the dynamic ranges of these developed sensors can be conveniently tuned by adjusting the amount of aggregation reagents. For example, Du *et al.* [44] proposed a flexible colorimetric sensor for Hg^{2+} composed of Au NPs and oligopeptides. As shown in Fig. 6, in the absence of Hg^{2+}, the addition of oligopeptides to the Au NPs solution resulted in the aggregation of Au NPs. In contrast, in the presence of Hg^{2+}, the aggregated Au NPs returned to a dispersion state, because oligopeptides had stronger affinity with Hg^{2+} than that with Au NPs. Similarly, 4,4'-dipyridyl (DPy) [45], 4-mercaptobutanol (4-MB) [47], pyridine [48], cysteine [49,50] and thymine [51] were used as aggregation reagents for the development of colorimetric sensors for Hg^{2+} based on the

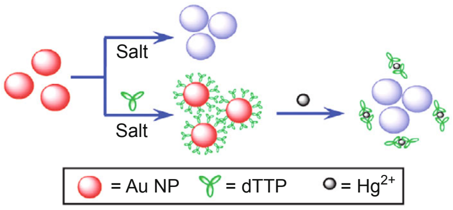

Figure 5 Schematic description of the colorimetric sensing of Hg^{2+} based on the dTTPs-stabilized Au NPs. Reproduced with permission from Ref. [43]. Copyright 2011, Royal Society of Chemistry.

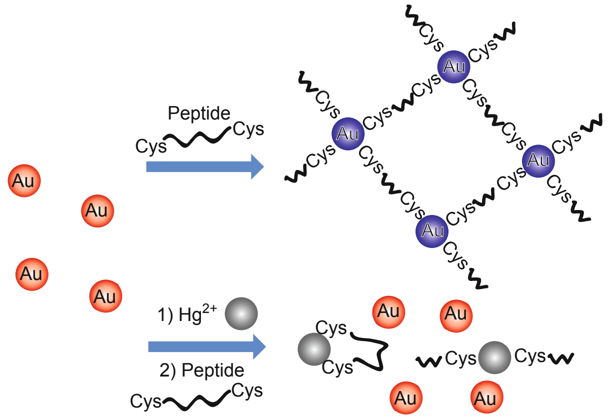

Figure 6 Colorimetric detection of Hg^{2+} based on simply mixing Au NPs and oligopeptides. Reproduced with permission from Ref. [44]. Copyright 2011, Wiley-VCH Verlag GmbH & Co. KGaA.

anti-aggregation of Au NPs. All of these sensors showed high sensitivity and selectivity.

Also, Wu *et al.* [52] developed a colorimetric assay for Hg^{2+} using mercury-specific deoxyribonucleic acid-functionalized Au NPs as a colorimetric probe, based on the anti-aggregation of Au NPs induced by the formation of folding structure of T-Hg^{2+}-T complexes. Lou *et al.* [46] reported a "blue-to-red" colorimetric method for sensing Hg^{2+} and Ag^+ based on stabilization of Au NPs by redox formed metal coating in the presence of ascorbic acid (AA). When *N*-acetyl-L-cysteine was added to the Tween 20 modified Au NPs solution free of Hg^{2+} and Ag^+, the Au NPs aggregated with a red-to-blue color change. However, in the presence of Hg^{2+} or Ag^+, the ions were reduced by AA to form Hg-Au alloy or Ag coating on the Au NPs surface, which inhibited the aggregation of Au NPs with a color change from blue to red.

Ag NPs-based colorimetric assays

Ag NPs are also good candidates for Hg^{2+} colorimetric sensor design, because Ag NPs with different size and shape exhibit a wide range of colors owing to their SPR, which is similar to Au NPs. And in comparison with Au NPs, Ag NPs are more cost-effective and have higher extinction coefficients relative to Au NPs of the same size [53].

In the Ag NPs-based colorimetric assays for Hg^{2+}, the main detection mechanism is based on the redox reaction between Ag NPs and Hg^{2+}. Because the Standard Electrode Potential of Ag^+/Ag (0.80 V) is lower than that of Hg^{2+}/Hg (0.85 V), Hg^{2+} can react with Ag NPs to form metallic mercury [54]. The erosion reaction of Ag NPs by Hg^{2+} causes the changes in the SPR band, which allows the quantitative detection of Hg^{2+}. Our lab developed a colorimetric method for detection of Hg^{2+} based on starch-stabilized Ag NPs [55]. In the presence of Hg^{2+}, the color yellow of the Ag NPs changed to colorless, accompanied with the decrease and blue shift of SPR band (Fig. 7). The limits of detection (LOD) was estimated to be 5 ppb. Based on the same principle, Farhadi *et al.* [56] used unmodified Ag NPs as a colorimetric probe to detect Hg^{2+} with an LOD of 2.2×10^{-6} M. Bera *et al.* [57] synthesized polyhedral Ag NPs and used them as colorimetric probes for detecting Hg^{2+}. As shown in Fig. 8, the polyhedral Ag NPs show two bands, corresponding to the quadrupole and dipole in-plane plasmon resonance, respectively. With increasing Hg^{2+} concentration, the longer-wavelength band decrease gradually and then disappear, with a color change from deep green to bright yellow. The polyhedral Ag NPs transfer to spherical NPs due to oxidative etching. The sensor had a detection limit of 9 ppb. Ramesh *et al.* [58] fabricated Ag NP-embedded poly(vinyl alcohol) (Ag-PVA) thin film and used it as a selective sensor for Hg^{2+}, Hg_2^{2+} and Hg with an LOD of 1 ppb. This sensor can work *in situ* as well as *ex situ*. Apilux *et al.* [59] reported a colorimetric detection of Hg^{2+} using Ag NPs on a paper-based device, an LOD of 2 ppb could be achieved by using a pre-concentration scheme.

Besides the commonly used redox-reaction based colorimetric assays, very few colorimetric sensing system based on Hg^{2+}-induced Ag NPs aggregation were also reported. Wang *et al.* [60] developed a colorimetric detection of Hg^{2+} using Ag NPs and mercury-specific oligonucleotides (MSO). The presence of Hg^{2+} caused the conformation change of MSO from random coil structure to hairpin structure due to the formation of T-Hg^{2+}-T base

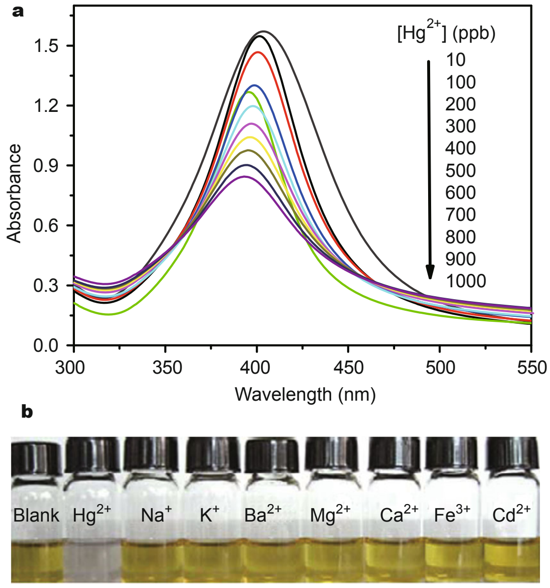

Figure 7 (a) UV-vis absorption response of Ag nanoparticles upon the addition of Hg^{2+} ions (10 ppb–1 ppm). (b) Color change of the Ag NPs in the presence of various representative metal ions (10^{-4} M). Reproduced with permission from Ref. [55]. Copyright 2009, Springer.

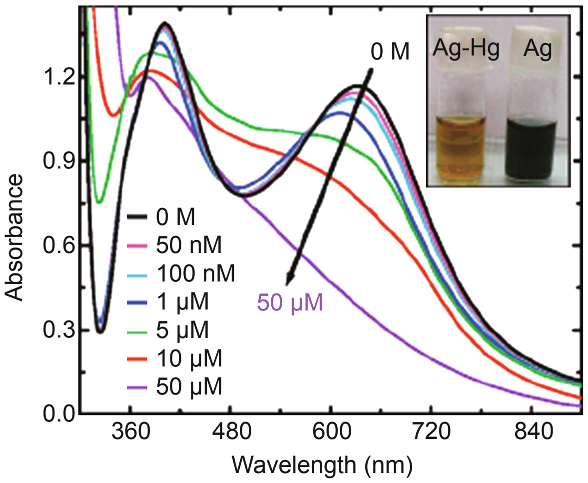

Figure 8 Optical spectra of polyhedral Ag nanostructures obtained at different concentrations of Hg (II) ions. Inset shows a photograph of colloidal Ag NPs in the absence and presence of Hg (II) (50 μM). Reproduced with permission Ref. [57]. Copyright 2010, American Chemical Society.

pairs, which resulted in the aggregation of Ag NPs with a yellow-to-red color change. Wang *et al.* [61] presented a dual functional colorimetric sensor for Hg^{2+} and H_2O_2 based on the catalytic reduction of Hg^{2+} to Hg by Ag NPs in the presence of H_2O_2, which caused the aggregation of Ag NPs. The addition of H_2O_2 to the mixture of Ag NPs and Hg^{2+} led to the color change from yellow to rose pink and a red shift of SPR band. This was because the formed Hg through the reduction of Hg^{2+} adsorbed on the surface of Ag NPs, which released citrate from the Ag NPs surface and thus caused the aggregation of Ag NPs. The introduction of H_2O_2 to the system improved the detection sensitivity. Besides, for the first time, our lab developed a facile colorimetric sensor for Hg^{2+} based on the anti-aggregation of 6-thioguanine-capped Ag NPs [62]. In the absence of Hg^{2+}, the addition of 6-thioguanine to Ag NPs solution led to the aggregation of Ag NPs with a yellow-to-reddish-brown color change. While the presence of Hg^{2+} inhibited the aggregation of Ag NPs with a reverse color change from reddish-brown to yellow. This method shows good potential for the colorimetric detection of heavy metal ions based on the anti-aggregation of Ag NPs.

Recently, Chen *et al.* [63] presented a new colorimetric approach for sensing Hg^{2+} based on the morphology transition of 1-dodecanethiol ($C_{12}H_{25}SH$)-capped Ag nanoprisms (NPRs) in the presence of excess I^-. The abstraction of $C_{12}H_{25}SH$ from the surface of Ag NPRs by Hg^{2+} allowed the bare surface silver atoms to be consumed by excess I^-, which led to the morphology transition from triangle to disk and the color change from blue to purple (Fig. 9). The LOD was 3.3 nM.

FLUORESCENT SENSORS

Fluorescent sensors are attractive due to their intrinsic advantages such as high sensitivity, rapidity, and multiplicity of measurable parameters [24]. Generally, fluorescent sensors provide higher sensitivity compared with the colorimetric sensors [64]. The fluorescent sensors can quantitatively detect analytes through analyzing the change of intensity and wavelength of fluorescence. Analytes induced “turn on” and “turn off” sensing mechanisms have been proposed in the fluorescence assays. Most Hg^{2+}-sensitive fluorescent sensors are turn-off types.

QDs based fluorescent sensors

The most common fluorescent NPs used in fluorescence based sensors are QDs. Due to the strong quantum confinement effect, QDs have size-tunable electronic transitions and strong fluorescence emission when the size approaches the Fermi-wavelength of conduction electrons [25]. In comparison with traditional organic dyes, QDs have unique optical properties such as broad excitation spectra, tunable narrow emission spectra, high quantum yields, long luminescence lifetime, negligible photo-bleaching and excellent chemical stability, making them more suitable for fluorescent sensing. The luminescence of

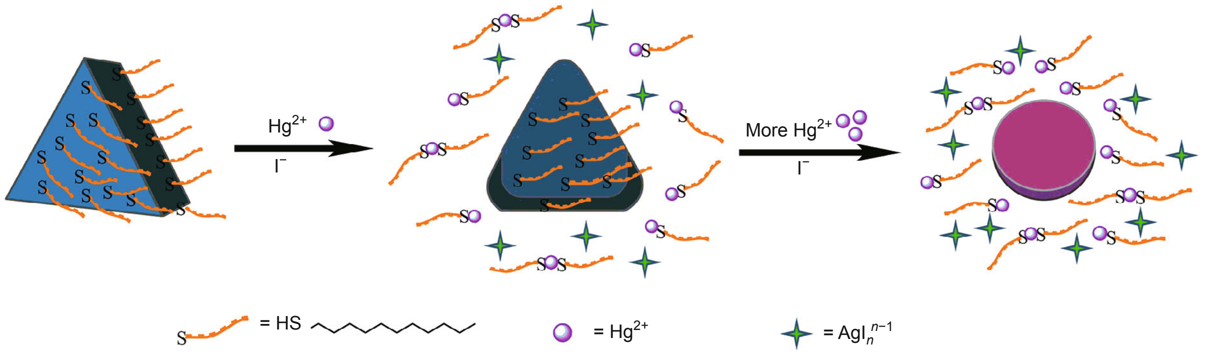

Figure 9 Schematic sensing mechanism of a Hg^{2+}-controlled morphology transition of 1-dodecanethiol-capped Ag NPRs in the presence of excess I^-. Reproduced with permission from Ref. [63]. Copyright 2014, American Chemical Society.

QDs is very sensitive to their surface states, and the physical or chemical interactions between the analytes and the surface of QDs lead to changes in the efficiency of the radiative electron-hole recombination, resulting in luminescence quenching or activation of QDs [65]. This behavior provides the basis for developing fluorescent sensor with QDs. Generally, the interaction of metal ions with QDs leads to a fluorescence quenching which can be explained by electron transfer process, ion binding interaction, inner filter effect and non radiative recombination pathway [66]. In some cases, fluorescence enhancement, which is usually attributed to the passivation of trap states or defects on the QDs surfaces, can also be observed.

Since Chen and Rosenzweig [66] first used water-soluble CdS QDs modified by different ligands (L-cysteine, thioglycerol and polyphosphate) as ion probes to detect copper and zinc ions in aqueous medium, several groups have employed QDs as chemical sensors for cations. And the QDs-based sensors for Hg^{2+} were the most studied. Nowadays, different Cd-chalcogenide QDs (CdS, CdSe, CdTe) coated with thiol-containing organic molecules such as L-cysteine (L-Cys), mercaptoacetic acid (MAA), mercaptopronionic acid (MPA), denatured bovine serum albumin (dBSA), cysteamine (CA) and thioglycolic acid (TGA) were synthesized and used as fluorescent probes to detect Hg^{2+} [67–72]. Besides the commonly used Cd-chalcogenide QDs, their derivatives such as MAA-capped CdS/ZnS core-shell QDs and QDs doped with rare earth ions (CdS:Eu QDs and CdS:Tb QDs capped with glutathione (GSH)) were also utilized for Hg^{2+} analysis [73–75]. The above mentioned sensing systems were all based on the fluorescence quenching of QDs by Hg^{2+}. And the fluorescence quenching mechanism was based on electron transfer process between QDs surface ligands and Hg^{2+} [68], or the quenching effect was explained by metal ion displacement between Cd^{2+} and Hg^{2+} on the QDs surface due to the higher binding affinity of Hg^{2+} to S^{2-}, Se^{2-} or Te^{2-} [67,76,77].

Li *et al.* [78] developed a fluorescence sensor for Hg^{2+} based on the nanometal surface energy transfer (NSET) in the CdSe/ZnS QDs/DNA/Au NPs ensemble with the LOD of 0.4 and 1.2 ppb in buffer solution and river water, respectively. When Hg^{2+} was present in the system containing DNA functionalized CdSe/ZnS QDs and Au NPs, QDs and Au NPs were brought into close proximity due to the formation of T-Hg^{2+}-T complexes, which resulted in the fluorescence quenching of QDs via NSET from QDs to Au NPs (Fig. 10). Similarly, based on the stable structure of T-Hg^{2+}-T, Huang *et al.* [79] described a time-gated fluorescence resonance energy transfer (TGFRET) sensing strategy using DNA functionalized Mn-doped CdS/ZnS QDs and Au NPs to detect Hg^{2+}. The proposed sensor showed detection limits of 0.49 nM in buffer and 0.87 nM in tap water samples.

As can be seen, nearly all of QDs-based sensors for Hg^{2+} were based on Cd-chalcogenide QDs (CdS, CdSe, CdTe). Considering the high toxicity of Cd, our group used low-toxic ZnS QDs as a substitute for Cd based chalcogenide QDs in the determination of Hg^{2+} [80]. Water-soluble ZnS QDs capped with *N*-acetyl-L-cysteine (NAC) were easily synthesized by a one-step process and used as a novel eco-friendly fluorescence sensor for Hg^{2+}. The quantitative detection of Hg^{2+} ions was developed based on fluorescence quenching of ZnS QDs with high sensitivity (5 nM) and selectivity (Fig. 11). The quenching mechanism was studied by both fluorescence and UV/vis absorption spectra, and it was assumed to be the effective electron transfer from

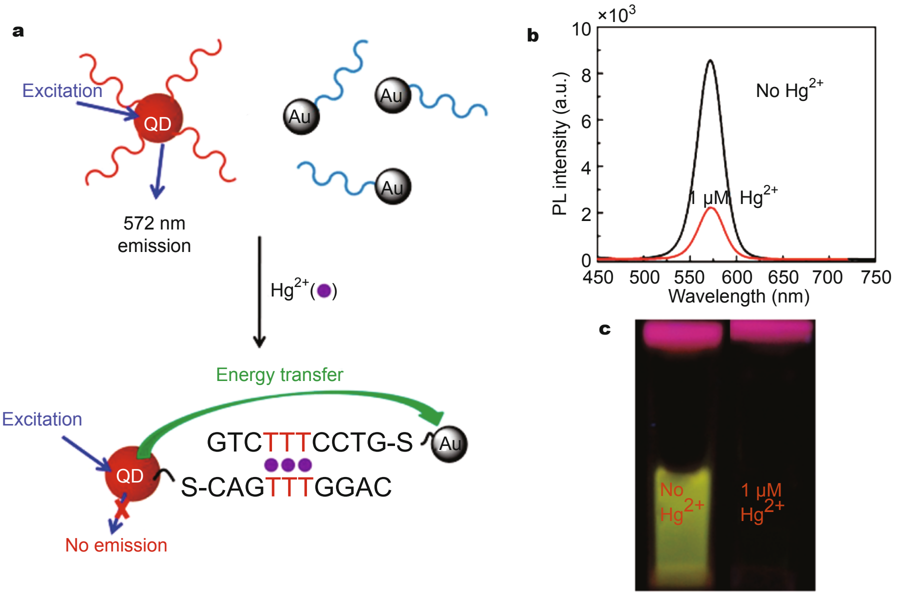

Figure 10 (a) Schematic illustration of the operating principle of the QD/DNA/Au NP ensemble sensor for Hg^{2+} detection. (b) Fluorescence emission spectra and (c) photograph under 365 nm laser excitation of the QD/DNA/Au NP solution (96 nM QDs, 104 nM Au NPs, and 0.1 mM ethylenediamine in 0.3 M phosphate buffered saline) before and after addition of 1 μM Hg^{2+}. Reproduced with permission from Ref. [78]. Copyright 2011, American Chemical Society.

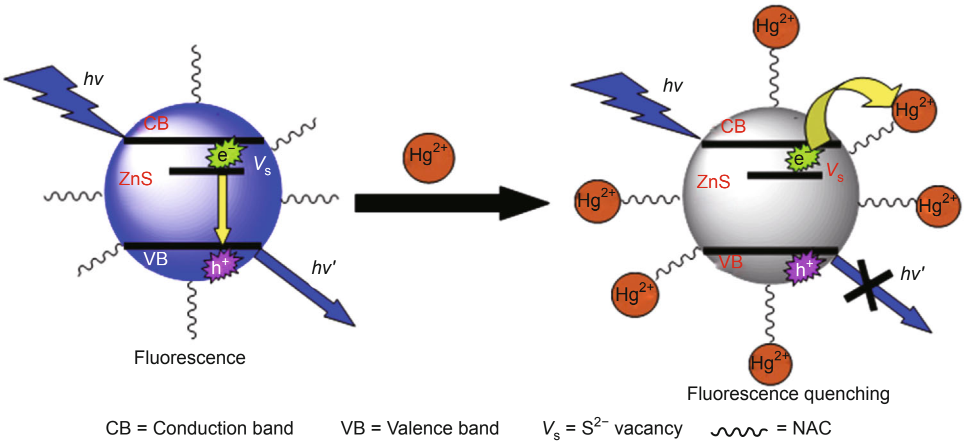

Figure 11 Illustration for the fluorescence quenching of NAC-capped ZnS QDs by Hg^{2+}. Reproduced with permission from Ref. [80]. Copyright 2011, Elsevier.

surface traps of ZnS QDs to Hg^{2+} ions.

As mentioned above, most of the developed QDs-based sensors for Hg^{2+} worked in a "turn off" mode. Compared with "turn-off" Hg^{2+} sensors, the "turn-on" sensing mode can offer advantage to reduce the likelihood of a false positive signal [81]. So, a "turn-on" sensor is preferred. There were few reports about fluorescence detection of Hg^{2+} based on the enhancement of QDs fluorescence. For instance, Zhu *et al.* [82] reported an Hg^{2+} sensor in the near-infrared region based on MAA-capped InP QDs, in which the fluorescence intensity was enhanced in the presence of Hg^{2+} because of the formation of HgS nanoparticles, which acted as electron–hole recombination centers. Huang *et al.* [83] presented a "turn-on" fluorescent sensor for Hg^{2+} based on single-stranded DNA functionalized Mn:CdS/ZnS QDs and Au NPs. As shown in Fig. 12, in the absence of Hg^{2+}, Au NPs functionalized with 10-mer single-stranded DNA (strand B) quenched the fluorescence of QDs functionalized with 33-mer thymine-rich single-stranded DNA (strand A) due to FRET. However, when Hg^{2+} was present in the sensing system, Hg^{2+}-mediated T-Hg^{2+}-T pairs led to the conformational change of strand A, resulting in the enhancement of fluorescence signal. The detection limit was as low as 0.18 nM.

Compared with general fluorescence, synchronous fluorescence spectroscopy (SFS) is a multidimensional fluorescence technique. This technique can maintain the sensitivity associated with general fluorescence. Besides, it can also offer several advantages such as simplification of emission spectra, improvement of the selectivity and spectral resolution and decreasing the interference owing to light scattering. More recently, synchronous fluorescence determination of Hg^{2+} based on GSH-capped CdS NPs [84] and denatured ovalbumin (dOB) coated CdTe QDs [85] was developed. The detection limits was 4.5 and 4.2 nM, respectively.

Metal NPs based fluorescent sensors

Both metal NPs and metal NCs are used for the development of fluorescent sensors. Metal NPs (Au NPs) can serve as excellent fluorescence quenchers for FRET-based assays because of their high molar extinction coefficients and broad energy bandwidth [14]. Unlike large metal NPs, small metal NPs (< 2 nm) was known as metal NCs consisting of a few to several hundred metal atoms lacking an apparent SPR band, but fluorescing more strongly [15]. They are emerging as an alternative to QDs due to their nontoxicity and good biocompatibility. Water-soluble Au NCs and Ag NCs have been synthesized and used as fluorescent sensors for Hg^{2+} with high sensitivity and selectivity.

In the Au NPs based sensing system, two sensing strategies were usually used. The first scheme was based on the quenching ability of Au NPs (13 and 32 nm) to the fluorescence of nearby fluorophores through non-radiative energy and electron transfer processes [86]. Darbha *et al.* [87] demonstrated the use of a rhodamine B (RB) protected Au NPs for sensitive detection of Hg^{2+} in soil, water and fish, with an LOD of 2 ppt. In their sensing system, the fluorescence of RB was quenched by nonradiative energy transfer to the Au NPs, while in the presence of Hg^{2+}, the fluorescence of RB enhanced dramatically due to its release from the surfaces of Au NPs, thus leading to a "turn-on" Hg^{2+} sensor. Based on the Hg^{2+}-induced conformational changes of a T-rich ssDNA and the difference in electrostatic affinity between ssDNA and double-stranded DNA (dsDNA) toward Au NPs, a colorimetric and fluorescent dual sensor for Hg^{2+}, using Au NPs and the fluorescein (FAM)-tagged ssDNA with mismatched T-T sequences, was presented by Wang *et al.* [88]. In the absence of Hg^{2+}, the FAM-tagged ssDNA protected the Au NPs from salt-induced aggrega-

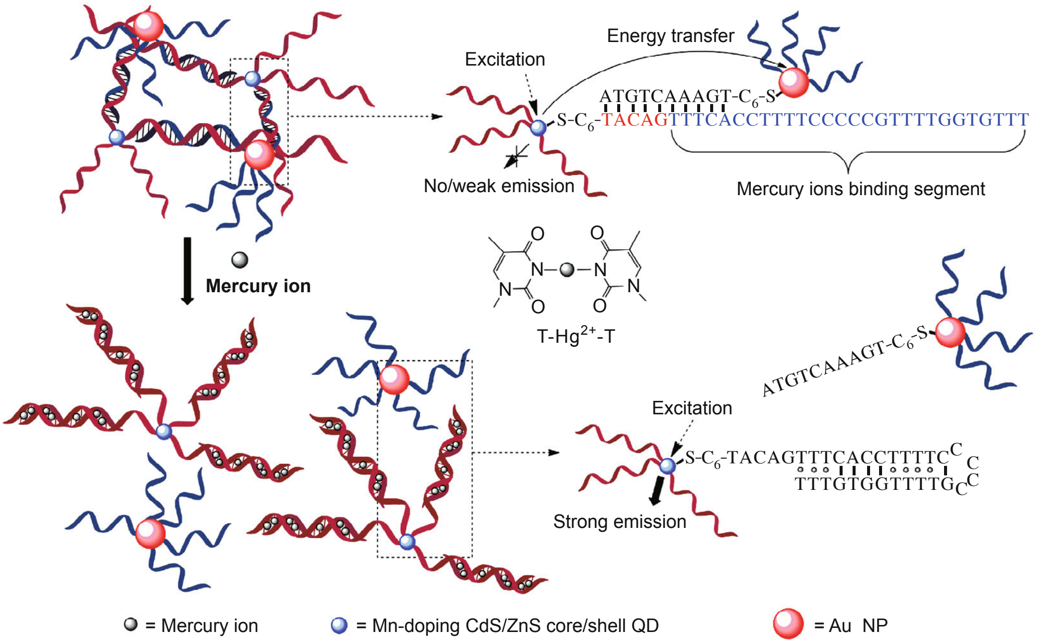

Figure 12 Schematic description of the "turn-on" fluorescent sensor for Hg^{2+} based on the Hg^{2+}-mediated formation in DNA duplexes. Reproduced with permission from Ref. [83]. Copyright 2013, American Chemical Society.

tion and the fluorescence of FAM was quenched through an FRET process. Upon the addition of Hg^{2+}, binding of Hg^{2+} with the ssDNA formed a dsDNA structure, causing the aggregation of Au NPs with a red-to-blue color change and fluorescence restoration of the FAM. The LOD of this assay was 40 nM.

The second frequently adopted scheme was based on the fluorescence quenching of Au NCs. Au NCs capped with lysozyme (Lys), bovine serum albumin (BSA) and dihydrolipoic acid (DHLA) have been synthesized for sensing Hg^{2+} through the specific interaction between Hg^{2+} ($5d^{10}$) and Au^{+} ($5d^{10}$) on the surface of Au NCs [89–93]. As shown in Fig. 13, the formation of the metallophilic bond of Hg^{2+}–Au^{+} can quench the fluorescence of Au NCs, which was used for the detection of Hg^{2+} with high sensitivity and selectivity [90]. Another kind of Au NCs-based fluorescent assay relied on the aggregation-induced fluorescence quenching of Au NCs by Hg^{2+}. 11-mercaptoun-

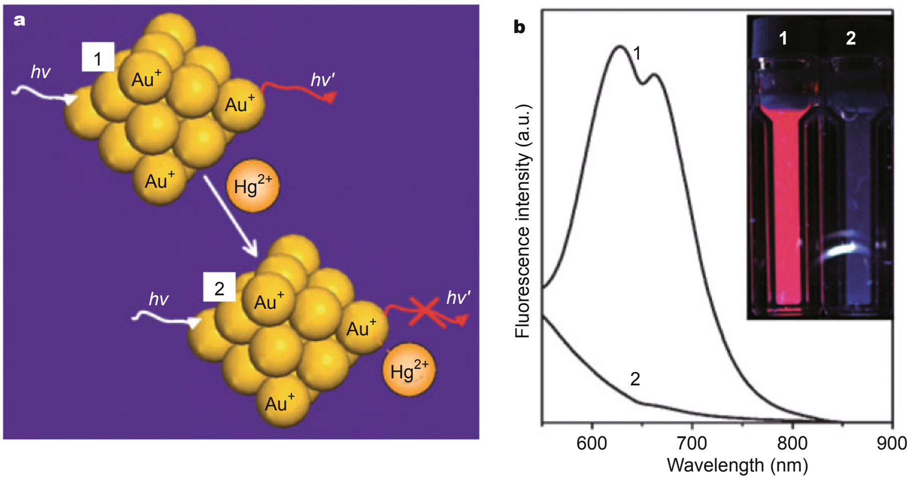

Figure 13 (a) Schematic of Hg^{2+} sensing based on the fluorescence quenching of Au NCs resulting from high-affinity metallophilic Hg^{2+}-Au^{+} bonds. (b) Photoemission spectra (λ_{ex} = 470 nm) and (inset) photographs under UV light (354 nm) of Au NCs (20 mM) in the (1) absence and (2) presence of Hg^{2+} ions (50 mM). Reproduced with permission from Ref. [90]. Copyright 2010, Royal Society of Chemistry.

decanoic acid protected Au NCs (11-MUA-Au NCs) were used as a fluorescent probe to detect Hg^{2+}. The interaction of Hg^{2+} with the acid groups induced the aggregation of 11-MUA-Au NCs, resulting in the fluorescence quenching of 11-MUA-Au NCs. An LOD of 5.0 nM was obtained [94].

For the Ag NPs based sensing assay which is similar to the Au NCs-based sensing principle, Ag NCs stabilized with oligonucleotide [95], dBSA [96], GSH [97,98], DHLA [99] were synthesized and used as fluorescent probes for the selective and sensitive detection of Hg^{2+}, based on the fluorescence quenching of Ag NCs due to the $5d^{10}(Hg^{2+})$-$4d^{10}(Ag^{+})$ metallophilic interaction [96,97] or the aggregation of Ag NCs induced by Hg^{2+} [98,99]. The detection limit could reach 0.1 nM [98,99]. Besides the "turn-off" Hg^{2+} sensors, Deng *et al.* [100] established a "turn-on" fluorescence sensor for Hg^{2+} using the Hg^{2+}-mediated T-T formation to strengthen the DNA duplexes and influence the configuration of Ag NCs-forming sequence. The detection limit was 10 nM. Tao *et al.* [101] used poly(acrylic acid)-templated Ag NCs as a platform for fluorescence "turn-on" detection of Hg^{2+} due to the changes of the Ag NCs state, with an LOD of 2 nM (Fig. 14). Recently, MacLean *et al.* [102] reported a ratiometric detection of Hg^{2+} using DNA stabilized Ag NCs with two emission peaks. The 620 nm red peak was quenched by Hg^{2+} while the 520 nm green peak increased. A detection limit of 4 nM Hg^{2+} was obtained.

CDs based fluorescent sensors

Fluorescent CDs are a fascinating class of recently discovered carbon nanomaterials with sizes below 10 nm, and they are becoming an attractive alternative for fluorescent sensor due to their low toxicity, good biocompatibility as well as abundant optical properties. Water-soluble CDs were synthesized via different approaches and used as environmentally friendly fluorescence sensors for Hg^{2+}, based on Hg^{2+}-induced fluorescence quenching of CDs due to facilitating nonradiative electron/hole recombination annihilation via electron or energy transfer [103,104].

Considering the existing synthesis methods suffering from involvement of complex post-treatment processes or the use of expensive reagents, it is highly desirable to develop new strategy toward rapid and green synthesis of CDs with high sensitivity for Hg^{2+} detection.

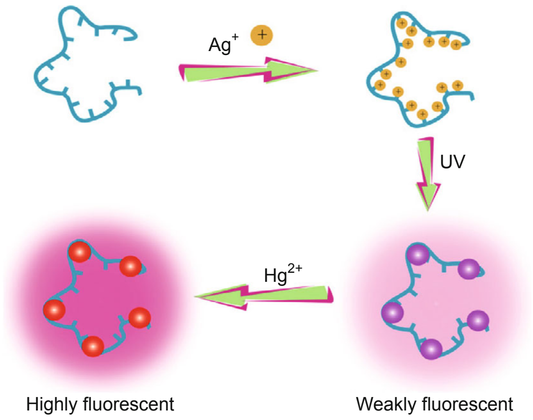

Figure 14 Schematic illustration of the poly(acrylic acid)-templated silver nanoclusters (PAA-Ag NCs) formation and the fluorescence and colorimetric response of the PAA-Ag NCs to Hg^{2+} ions. Reproduced with permission from Ref. [101]. Copyright 2012, Elsevier.

SERS SENSORS

SERS is a powerful analytical technique which can provide not only enhanced Raman signals of the molecules adsorbed on the metallic substrates, but also details of the molecular structures [105]. The localized surface plasmon resonance (LSPR) excitation of noble metal NPs enhances the local electromagnetic fields at the NP surface, which forms the basis of SERS enhancement [13]. For SERS applications, Ag NPs and Au NPs with diverse morphologies are the primary materials as excellent SERS substrates, due to their optical response in the visible region of the electromagnetic spectrum. SERS sensor as an alternative to commonly used optical sensor has been widely applied in high-sensitive analysis of environmental pollutants because it can detect the analytes even on a single-molecule level [106]. Up to now, only very few SERS sensors for Hg^{2+} either performed on solid substrate or in aqueous solution have been reported (Fig. 15). Based on the decrease or increase of SERS intensity induced by the interaction between Hg^{2+} and surface bound Raman reporter molecules, a quantitative detection of Hg^{2+} could be developed.

For the SERS assay performed on solid substrate, the Raman signals of the Raman reporter molecules are associated with the distance between the Raman reporter molecules and the substrate surface. If the interaction between Hg^{2+} and surface bound Raman reporter molecules enable the Raman reporter molecules get close to the substrate

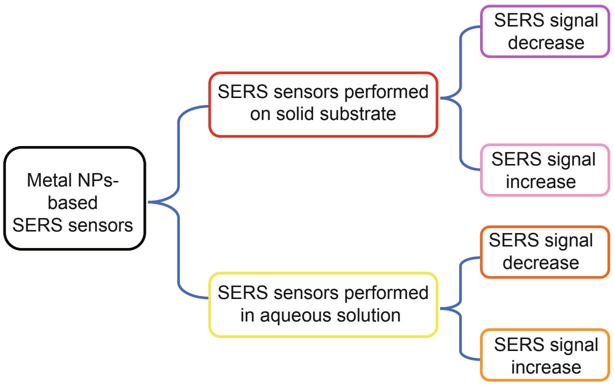

Figure 15 Sensing strategies of the metal NPs as SERS sensors for Hg^{2+}.

surface, the Raman signals of the Raman reporter molecules would be enhanced. On the contrary, if the addition of Hg^{2+} displaces the Raman reporter molecules from the substrate surface due to the strong coordination between Hg^{2+} and Raman reporter molecules, the decrease in the Raman signals of the Raman reporter molecules would be observed. For example, an ultrasensitive Au nanowire-on-film surface-enhanced resonance Raman scattering (SERRS) sensor for Hg^{2+} based on T-Hg^{2+}-T coordination chemistry was reported by Kang *et al.* [107]. As shown in Fig. 16, after adding Hg^{2+}, Trich DNAs folded into a hairpin structure to form stable T-Hg^{2+}-T complexes. As a result, the Raman reporter molecule cyanine dye (Cy5) got close to the Au nanowire-on-film, increasing the SERRS signal of Cy5. The sensor provided an LOD of 100 pM and good reproducibility. Based on the displacement principle, Zhang *et al.* [108] reported an extremely sensitive SERRS sensor for Hg^{2+} detection by using nanoporous gold (NPG) as a substrate and Cy5-labeled aptamer as optical tags. The formation of T-Hg^{2+}-T complex pulled the Cy5 tags away from the NPG substrate, leading to the decrease in the SERRS signal of Cy5. This Cy5-labeled aptamer@NPG SERRS sensor for Hg^{2+} has high sensitivity (1 pM) and selectivity. Grasseschi *et al.* [109] developed SERS spot tests to detect heavy metal ions, below 10^{-5} M, only Hg^{2+} could displace dithizone from the surface of the Au NPs, resulting in the decrease of the Raman signals. The LOD was 0.5 pg of Hg^{2+}. Similarly, Ma *et al.* [110] used para-aminothiophenol coupled Au NPs (PATP-Au) multilayer as SERS probes to detect Hg^{2+} with an LOD of 1 nM. Recently, Du *et al.* [111] reported a SERS chip for the femtomolar (fM) detection of Hg^{2+} by the assembly of Au@Ag NPs on a piece of silicon wafer followed by modification with DPy. The formation of Hg^{2+}-DPy complex leads to the release of DPy from the monolayer of Au@Ag NPs, thus quenching the Raman signal of DPy (Fig. 17). The LOD is as low as 1.0×10^{-14} M.

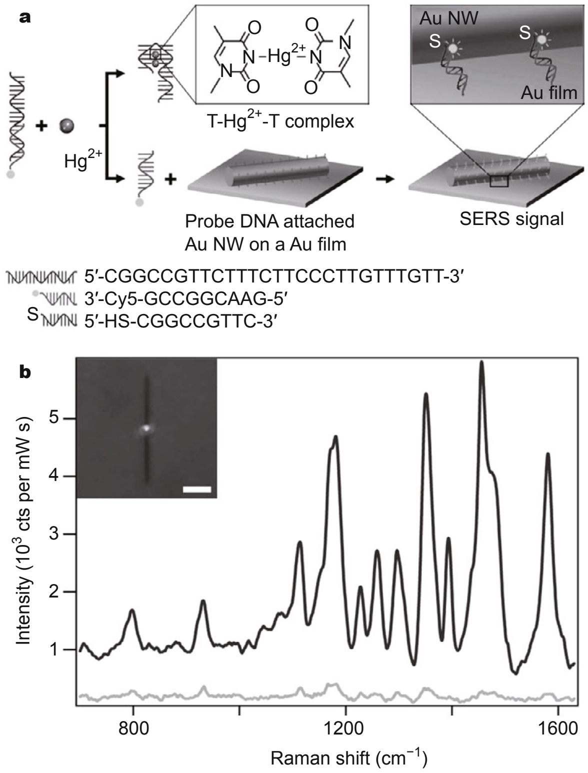

Figure 16 (a) Schematic representation of a SNOF SERRS sensor for Hg^{2+} detection based on a structure-switching dsDNAs. (b) SERRS spectra of a SNOF sensor in the absence of (bottom spectrum) and addition of 1 mM Hg^{2+} solution (top spectrum). The inset is an optical image of a SNOF sensor. The scale bar denotes 5 μm. Reproduced with permission from Ref. [107]. Copyright 2012, Royal Society of Chemistry.

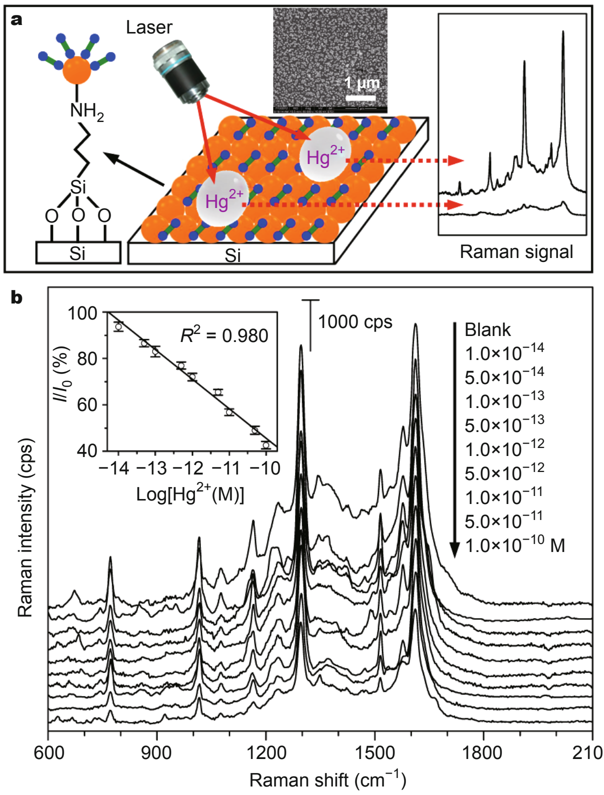

Figure 17 (a) Schematic drawing for direct detection of Hg^{2+} with the SERS chip fabricated by the assembly of Au@Ag NPs on a silicon wafer. (b) Evolution of SERS spectra of DPy with the addition of an aqueous Hg^{2+} droplet. The inset is the linear correlation of Raman intensity (at 1614 cm^{-1}) with the logarithm of Hg^{2+} concentrations from 1.0×10^{-14} to 1.0×10^{-10} M. Reproduced with permission from Ref. [111]. Copyright 2013, American Chemical Society.

In comparison with the above mentioned SERS sensor performed on solid substrate, the SERS sensor performed in aqueous solution is more suitable for quantitative detection of Hg^{2+}, due to the easy preparation and stability of liquid substrate. When the solution-phase metal NPs aggregate, intense electric fields known as "hot spots" can occur at the junctions of metal NPs, where the Raman signals are greatly enhanced due to electromagnetic and chemical enhancement factors. This property allows the aggregated metal NPs to be used as SERS-active substrates which exhibit high sensitivity [13]. In the SERS assay operated in aqueous solution, there are two main kinds of detection routes. One is based on Hg^{2+}-induced removal of Raman reporters from the aggregated metal NPs substrate surface or Hg^{2+}-inhibited aggregation of metal NPs, which results in the SERS signal decrease of the Raman reporters. The other is dependent on aggregation-induced SERS signal increase of the Raman reporters upon addition of Hg^{2+}.

Wang *et al.* [112] developed a SERS detection of Hg^{2+} in aqueous environment within a droplet-based microfluidic system based on RB-adsorbed Au NPs. The addition of RB to the Au NPs solution led to the aggregation of Au NPs. As a result, "hot spots" were formed and strong SERS signal of RB was observed. However, the SERS signal decreased gradually with increasing Hg^{2+} concentration, because the RB molecules were replaced by Hg^{2+} from the Au NPs surface. Quantitative detection of Hg^{2+} could be achieved by using the droplet-based microfluidic system and the LOD was between 100 and 500 ppt. Li *et al.* [113] proposed a SERS method for quantitative analysis of Hg^{2+} using 4-mercaptopyridine (MPy)-aggregated nanosilver as probe. In the presence of NaCl, the Ag NPs were aggregated, and MPy that adsorbed on the aggregated Ag NPs surfaces showed strong SERS signal. Upon addition of Hg^{2+}, the SERS intensity decreased due to the formation of $[Hg(MPy)_2]^{2+}$ complex. This group also used rhodamine 6G-aggregated nanosilver (ANS-Rh6G) as SERS probe for detecting Hg^{2+} by using cetyltrimethyl ammonium bromide (CTMAB) as aggregation reagent and rhodamine 6G as SERS reporter molecule (Fig. 18) [105]. Similarly, an SERS determination of Hg^{2+} with 2-mercaptoethanesulfonate modified Ag NPs was described by Chen *et al.* [114]. Our group designed a colorimetric and SERS dual-signal sensor for Hg^{2+} by facilely mixing Bismuthiol II and Au NPs, without dye tag [115]. In our sensing system, Bismuthiol II was used as both aggregation reagent and SERS reporter molecule. The addition of Bismuthiol II to the Au NPs solution led to the aggregation of Au NPs and strong SERS signal of Bismuthiol II was observed. However, the Bismuthiol II-induced aggregation of Au NPs could be reversed by Hg^{2+}, resulting in the SERS signal decrease.

Based on aggregation-induced SERS signal increase of the Raman reporters, Li *et al.* [116] developed an SERS detection of Hg^{2+} using L-cysteine-functionalized Ag NPs attached with Raman-labeling molecules 3,5-dimethoxy-4-(60-azobenzotriazolyl)pheno, with an LOD of 1 pM for Hg^{2+}. The coordination between the L-cysteine and Hg^{2+} formed an "inner complex salt", which resulted in

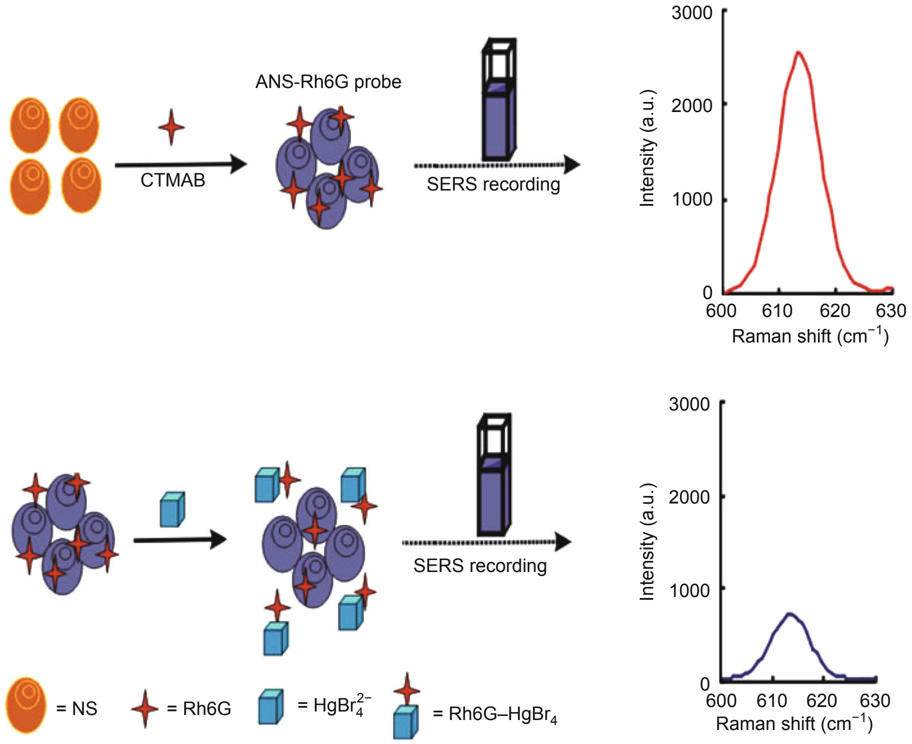

Figure 18 Principle of the ANS-Rh6G SERS probe detection of Hg^{2+}. Reproduced with permission from Ref. [105]. Copyright 2012, Springer.

the aggregation of Ag NPs. Consequently, the SERS signal increased (Fig. 19). Wang *et al.* [117] synthesized dandelion-like Au/polyaniline (PANI) composite nanospheres and used them as SERS sensors for Hg^{2+} detection based on the SERS signal increase of PANI. In this system, the strong interaction between Hg^{2+} and PANI weakened the interaction between PANI and Au NPs, leading to the aggregation of Au NPs. The developed SERS sensor showed high sensitivity (as low as 10^{-11} M) and good reproducibility. Lee *et al.* [118] reported a SERS sensor for recognition of Hg^{2+} down to 5 nM using aptamer-conjugated Ag NPs. In the presence of Hg^{2+}, the strong binding between Hg^{2+} and thymine-thymine base pairs led to a conformational rearrangement of the aptamer to form a hairpin structure. As a result, the Ag NPs aggregated and the SERS signal was increased.

Besides the regular spherical metal NPs, metal NPs with other shapes can also be used as SERS-active substrates for Hg^{2+} detection in aqueous solution. Metal NPs with complex sharp structure or more edges have higher SERS activity than spherical metal NPs [119]. Senapati *et al.* [120] developed a tryptophan protected popcorn shaped Au NPs based SERS probe for detecting Hg^{2+} with low detection limit (5 ppb) in aqueous solution. In the presence of Hg^{2+}, tryptophan is released from popcorn shaped Au NPs and the popcorn shaped Au NPs lose their sharp edges due to the formation of a stable complex between Hg^{2+} and tryptophan, and as a result, the SERS signal of tryptophan decreased. This SERS sensor is able to determine Hg^{2+} in the alkaline battery. Recently, Ma *et al.* [121] developed an SERS sensor for Hg^{2+} detection using self-assembled gold nanostar dimer. The mismatch of the T-Hg^{2+}-T base pair led to the formation of self-assembled gold nanostar dimer, providing ultrasensitive SERS enhancement for Hg^{2+} detection with an LOD of 0.8 pg mL^{-1}.

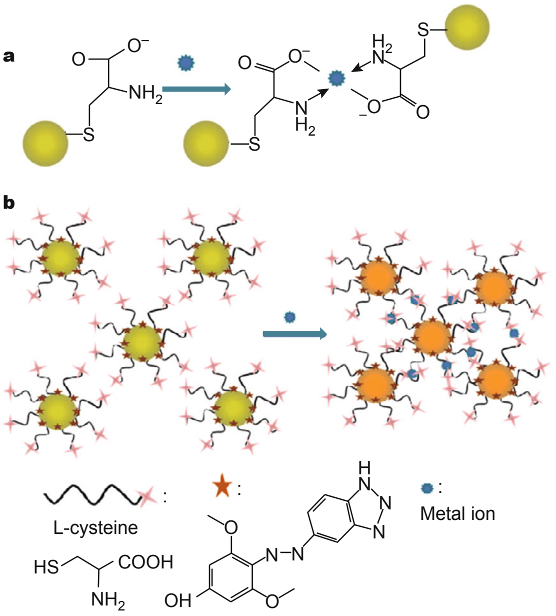

Figure 19 (a) Schematic representation of the formation of coordination compounds between L-cysteine (absorbed on Ag nanoparticles) and metal ions. (b) Schematic illustration of the aggregation of Ag nanoparticles induced by metal ions. Reproduced with permission from Ref. [116]. Copyright 2013, Elsevier.

Notably, the above mentioned SERS sensors for Hg^{2+} were developed according to the change of SERS intensity. Considering that many factors could affect the SERS intensity in SERS detection, the SERS methods for Hg^{2+} detection employing SERS intensity ratios of related bands were developed. A trimercaptotriazine (TMT)-modified Au NPs based SERS sensor for Hg^{2+} and Cd^{2+} in aqueous solution was developed by Zamarion *et al.* [122]. This sensor allowed the quantitative detection of Hg^{2+} and Cd^{2+} by using relative SERS intensity ratios of the selected bands. A linear range of 2×10^{-7}–2×10^{-6} M for Hg^{2+} was obtained. Similarly, Tan *et al.* [123] reported an SERS sensor for multiple heavy metal ions based on 2-mercaptoisonicotinic acid modified Au NPs. Hg^{2+} and Pb^{2+} could be detected by using relative peak intensity ratios, with detection limits of 3.4 $\times10^{-8}$ and 1.0 $\times10^{-7}$ M, respectively.

CONCLUSIONS

This review described NP-based optical sensors that allow the sensitive and selective detection of Hg^{2+} through colorimetric, fluorescence and SERS assays. These optical sensors were classified into several different categories according to their detection routes or sensing mechanisms. Compared with conventional sensors, the NP-based optical sensors have shown numerous advantages such as high sensitivity, super selectivity, simplicity, rapidness and low cost. There still exist some limitations in practical application. In the colorimetric assay, most functionalized metal NPs are unstable in complex environmental samples such as river water, lake water and sea water, because the high concentrations of salt in these complex samples can cause different levels of aggregation of metal NPs. Besides, the sensitivity of colorimetric sensors is generally insufficient for the detection of Hg^{2+} in the real world. In the fluorescence assay, although high sensitivity can be provided relative to the colorimetric assay, the commonly used fluorescent nanomaterials suffer from the involvement of toxic reagents such as Cd and Pb. It is still highly desired to develop non-toxic fluorescent nanomaterials as novel eco-friendly sensor for Hg^{2+}. Fluorescent metal NPs (Au NCs and Ag NCs) and CDs are emerging as popular fluorescent probes for their high biocompatibility and low toxicity. From the point of view of the practical applications of NCs and CDs, the development of new strategy toward rapid and green synthesis of highly fluorescent NCs and CDs with high sensitivity for Hg^{2+} detection is highly needed. SERS sensor as an alternative to commonly used optical sensor is still in the burgeoning stage, to overcome the problems of quantitative analysis in SERS assay, the development of reliable, stable and easily prepared SERS substrates with reproducibility is still a challenge. Now, the practicality of NP-based optical sensors for Hg^{2+} is usually limited to simple systems, but we believe that there will be a tremendous growth in the development of NP-based sensor devices for real-life applications in the near future.

Besides the application of nanomaterials in the detection of Hg^{2+}, nanomaterials also offer the potential for the removal of Hg^{2+} from water samples, owing to their associated high reactivity, high surface area and strong adsorption ability. Nanomaterials such as metal NPs, magnetic NPs, carbon nanomaterials and semiconductor nanomaterials have been used for the removal of Hg^{2+} from aqueous solution [124,125]. For example, Ojea-Jimenez *et al.* [126] reported that citrate-coated Au NPs can remove Hg^{2+} from Milli-Q water and river water. Ag NPs supported on activated alumina could be used for the removal of Hg^{2+} present in the contaminated water at room temperature with high removal ability [127]. Qi *et al.* [128] synthesized water-soluble Fe_3O_4 superparamagnetic nanocomposites by coating hydrophobic magnetite superparamagnetic nanoparticles with functional amphiphilic oligomers. The obtained Fe_3O_4 superparamagnetic nanocomposites could efficiently remove low concentrations of Hg^{2+} from water samples by low-field magnetic separation. Three different functionalized multiwalled carbon nanotubes were synthesized for the removal of Hg^{2+} over a wide range of pH (6–9) values [129]. Qu *et al.* [130] prepared ZnS nanocrystals sorbent via direct coating ZnS nanocrystals on the surface of α-Al_2O_3 NPs. The as-prepared ZnS nanocrystals sorbent was used for the removal of Hg^{2+} based on size-dependent cation exchange. The saturated adsorption capacity was about 2000 mg g^{-1}. Recently, Kandjani *et al.* [131] reported SERS-active ZnO/Ag nanoarrays that can detect Hg^{2+}, remove Hg^{2+} and can be regenerated over many cycles. From the point of practical applications, the ideal nanomaterials for Hg^{2+} removal should meet the following features: (1) environment security, (2) low cost, (3) strong absorption capacity and (4) possessing either ion exchange sites or lattice vacancies.

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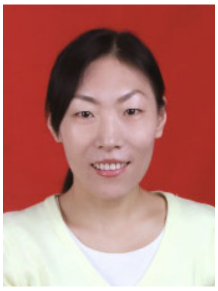
Conflict of interest The authors declare that they have no conflict of interest.



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中文摘要　汞离子(Hg^{2+})即使在微量浓度下也会给人类健康和环境带来危害, 因此发展快速、经济、具有高灵敏度和高选择性检测汞离子的方法是非常重要的. 纳米材料由于其优异的光学特性, 为环境中检测痕量汞离子的光学传感器的设计提供了一种强有力的手段. 基于纳米材料的光学传感器具有简单、快速、经济、灵敏等优异特性. 本文综述了利用功能化纳米材料(包括贵金属, 金属团簇, 半导体量子点和碳点)检测汞离子的光学方法的最新进展, 分别描述了比色法、荧光法和表面增强拉曼散射法对汞离子的检测路线, 和每种检测方法的检测原理, 最后讨论了未来发展基于纳米材料检测汞离子的光学传感器的前景和挑战.