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Detection of chemical pollutants in water using gold nanoparticles as sensors: a review

Abstract: Rapid and accurate evaluation of pollutant contamination in water is one of the key tasks of environmental monitoring. To make onsite assessment feasible, the analytical tools should be easy to operate, with minimal sample preparation needs. Gold nanoparticle (AuNP)-based sensors have the potential to detect toxins, heavy metals, and inorganic and organic pollutants in water rapidly with high sensitivity, and they are expected to play an increasingly important role in environmental monitoring. In this article, the synthesis, fabrication and functionalization of AuNPs are discussed, and the recent advances in the development and application of AuNP-based sensors for the determination of various pollutants contamination in water are reviewed.

Keywords: chemical pollutants; detection; gold nanoparticle.

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Introduction

Chemical pollution in water is one of the major environmental problems in today's world, since polluted water poses a threat to human health and welfare, and hinders the sustainable development of both society and the economy. The presence of chemical toxins, heavy metals, inorganic and organic pollutants in water, due to either natural or artificial processes (Duan et al. 2007, Wang et al. 2010), needs to be monitored constantly to safeguard the supply of clean drinking water to the public, and to control the impact on the environment and the ecosystem. In recent years, the combination of nanotechnology, chemistry, physics and biology, has allowed the development of ultrasensitive detection and imaging methods, including applications in electronic, magnetic, environmental, pharmaceutical, cosmetic, energy, optoelectronic, catalytic, and material fields (Auffan et al.

2009, Wang and Ma 2009, Wang et al. 2010). For the past decade, the field of environmental monitoring has seen the application of nanoparticles (NPs) being utilized as functional probes for analyzing toxins, metal ions, and inorganic and organic pollutants (Cheon and Lee 2008, Wang and Ma 2009). NPs, usually with a size between 1 and 100 nm, display unique properties not found in bulk-sized materials, mainly due to the strong physical confinement of electrons or holes in the NPs at the nanoscale. From a sensing perspective, the small size of NPs gives them large surface-to-volume ratios, which lead to rapid responses and high sensitivity. In addition, the physical properties of NPs (i.e., optical, electronic, magnetic properties) can be fine-tuned through control of their size, composition, shape, and surface chemistry, to generate highly functional molecular probes (Wang and Yu 2012). Surface-modified nanoparticles, such as gold and silver NPs (AuNPs/AgNPs) (Yu and Irudayaraj 2007, Xiao and Yu 2010, Wang and Yu 2012), quantum dots (QDs) (Peng et al. 2000, Peng and Peng 2001, Qu et al. 2001), magnetic NPs (MNPs) (Sun et al. 2006, Aurich et al. 2007, Kim et al. 2007, Taktak et al. 2007, 2008, Koh et al. 2008, Lowery et al. 2008) and carbon nanotubes (Shim et al. 2008, Zhang et al. 2010) can have specific target-binding properties that allow highly selective and sensitive target detection. As shown in Figure 1 (Peng et al. 2009), different types of NPs demonstrate different optical, fluorescence and magnetic properties, and interactions between these properties give NPs great potential for environmental screening. In this article, we focus on the application of AuNPs on the detection of waterborne chemical pollutants.

The unique optical properties of AuNPs come from the collective oscillation of electrons at their surfaces, known as surface plasmon resonance (SPR). Surface plasmons (SPs) are coherent electron oscillations that are excited by electromagnetic (EM) radiation at the metal-dielectric interface. The characteristics of such light-metal interactions are determined by the properties of the metal, the dielectric environment, and the frequency of the EM radiation. When the frequency of the SP resonates with that of the excitation radiation, SPR will occur at the metal-dielectric interface (Maier and Atwater 2005, Ozbay 2006, Atwater 2007). The SPR

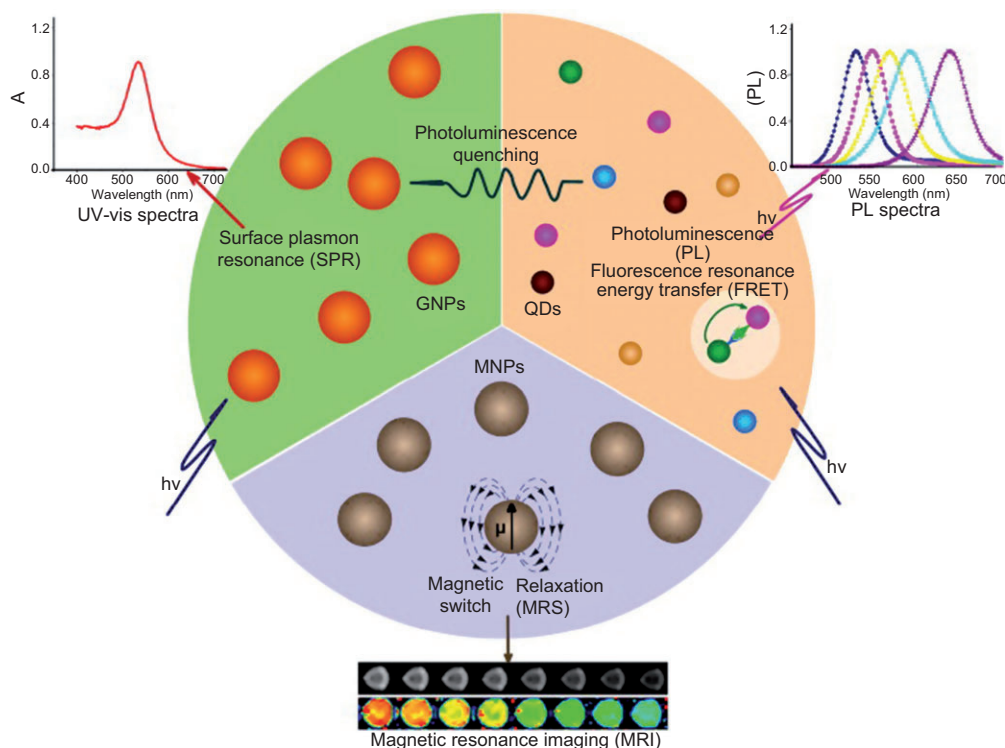


Figure 1 A schematic illustration of the properties of gold nanoparticles (AuNPs), quantum dots (QDs), and magnetic NPs (MNPs) for sensing applications (Peng et al. 2009). Copyright Elsevier B.V. and reproduced with permission.

frequency is determined by the size, shape and chemical composition of the metallic NPs. For spherical AuNPs, the resonance frequency lies in the visible region of the electromagnetic spectrum (Maier and Atwater 2005). Since AuNPs have a high surface area-to-volume ratio, the SPR frequency is exquisitely sensitive to the dielectric (refractive index) nature of its interface with the local surrounding medium (Wang et al. 2010). Any changes to the environment of these particles (i.e., surface absorption/desorption of chemical reagents, aggregation, medium refractive index, etc.) will shift the SPR frequency and result in a colorimetric change that can be utilized as signals for detection (Murphy 2002, Niemeyer and Simon 2005, Yu and Irudayaraj 2007). Detection schemes also often utilize the effect of enhancement on the local EM field surrounding the AuNPs caused by SPR. These enhancements, surface-enhanced Raman scattering (SERS) being one example, can lead to extraordinary sensitivity in chemical sensing; the detection level of a single target molecule has been reached in SERS (Kneipp et al. 2006). Further development in nanofabrication methodologies and sensor instrumentation will lead to much wider applications of these extremely sensitive nanosensors outside research laboratories (Lee and El-Sayed 2006, Stewart et al. 2008).

AuNPs have also been utilized in electrochemical sensing applications, where the AuNPs are deposited onto the surface of electrodes to improve the sensitivity of their electrochemical responses to the absorption of analytes (i.e., heavy metal ions, toxin species, etc.) (Dai and Compton 2006, Martínez-Paredes et al. 2009). With the AuNP-induced enhancement to the electrochemical signaling, ppb level limits of detection (LOD) have been achieved for a variety of environmental pollutants (Dai and Compton 2006, Martínez-Paredes et al. 2009).

Synthesis/fabrication and functionalization of AuNP probes

The synthesis and fabrication of metallic nanomaterials and nanostructures has been a very active research field for many years, due to their importance in many applications, including photonics and optoelectronics (Maier and Atwater 2005, Weeber et al. 2005, Dionne et al. 2006, Ozbay 2006, Satuby and Orenstein 2007), electronics (Blümel et al. 2007, Herderick et al. 2007), chemical and biological sensing (Gao et al. 2007, Lee et al. 2007), and medical diagnosis and therapies (Loo et al. 2005, Huang

et al. 2006b, Durr et al. 2007). As of today, the chemical and physical properties of metallic nanomaterials and nanostructures can be fine-tuned by controlling their sizes, shapes, and compositions (Murphy et al. 2005, Lu et al. 2006, Wiley et al. 2006). Many methods have been developed to make isotropic and anisotropic gold nanostructures with well-controlled sizes and shapes (Murphy et al. 2005, Stewart et al. 2008, Wang and Yu 2012). These approaches can be summarized into two categories, top-down and bottom-up (Stewart et al. 2008). Top-down techniques involve using various forms of conventional lithographic techniques to pattern nanostructures (e.g., on to planar substrate), whereas in bottom-up methods, nanostructures are “built” or “assembled” from atoms, molecules, and/or more complex mesoscale objects (Prikulis et al. 2004, Haes et al. 2005, Hicks et al. 2007, Stewart et al. 2008). Freely-floating AuNP colloids are usually made through the bottom-up approach. A typical bottom-up wet-chemistry synthesis of spherical nanoparticles of noble metals, involves the reduction of its metal salt in a solution and proceeds in two stages (Roucoux et al. 2002, Khomutov and Koksharov 2006). In the first stage, metal ions are reduced to metal atoms, which then undergo rapid collisions to form stable icosahedral nuclei of 1–2 nm in size. The initial concentration of nuclei depends on the concentration of the reducing agent, the solvent, temperature, and reduction potential of the reaction. This stage typically gets completed in a few seconds and determines the heterogeneity in the sizes and shapes of the NPs. Further growth of the NPs occurs in the second stage, by the reduction of metal ions on the surface of the nuclei until all ions are consumed. Simultaneously, a stabilization reaction is occurring, whereas a stabilizing agent is added on to the surface of the NPs to prevent them from aggregation, either through Coulombic repulsion (Pillai and Kamat 2004, Ott and Finke 2006) or steric hindrance (Roucoux et al. 2002, Anand et al. 2006). For example, AuNPs are often stabilized by thiol-capping agents (Yu and Irudayaraj 2007) that impart negative or positive charges to the particles.

The reduction of the metal salt can be carried out electrochemically (Plieth et al. 2005, Huang et al. 2006a, 2007, Starowicz et al. 2006), photochemically (Pillai and Kamat 2004, McGilvray et al. 2006, Sakamoto et al. 2007, Zhu et al. 2007), sonochemically (Jiang et al. 2004, Park et al. 2006), or using chemical reductants such as citrates (Pillai and Kamat 2004), hydrides (Kariuki et al. 2004, Pal et al. 2007), alcohols (Wiley et al. 2004), hydrogen (Evanoff and Chumanov 2004), hydroxylamine (Yuan et al. 2007), or hydrazine (Shi et al. 2006). By choosing a specific reductant, stabilizer, temperature, and

concentrations of the reactants, the shapes and sizes of the NPs can be controlled, as shown in Figure 2. For example, gold nanorods are often produced using wet-chemistry approaches (Jana et al. 2001, Murphy et al. 2005, Iqbal et al. 2007, Kanaras et al. 2007, Xiong et al. 2007). Typically, for making Au nanorods, a growing solution is prepared containing Au salt, a mild reducing agent (e.g., ascorbic acid), a surfactant stabilizer [e.g., cetyltrimethylammonium bromide (CTAB)], and other additives (e.g., AgNO_3); a NP “seed” (2–4 nm) is then added to the growth solution, and the Au salt is reduced on the surface of the seeds (Jana et al. 2001). Because CTAB binds to the side faces of the growing NP (due to favorable packing of Au atoms) more strongly and slows down the growth along the transverse axis, the growth along the longitudinal axis outpaces it and the NPs eventually become anisotropic and grow into a rod shape (Jana et al. 2001). The morphology, aspect ratio, and yield of rods are controlled by the composition and concentrations of the surfactant(s), additives, seeds, Au salts, and the reducing agent (Jana et al. 2001, Sau and Murphy 2004, Murphy et al. 2005, Ha et al. 2007, Iqbal et al. 2007, Yu et al. 2007). Because the longitudinal plasmon mode of nanorods can be tuned by adjusting the aspect ratio, they are particularly useful in photonics and sensing applications.

To make plasmonic AuNPs into useful nanosensors for chemical detection, it is necessary to add functionality to them through a functionalization process. This is particularly true for NPs made through wet-chemistry synthesis: the surfactant stabilizer needs to be replaced by a chemically active layer to which further attachment of functional molecules such as antibodies and DNAs can be performed.

The first step in a functionalization process is to chemically modify the surface of the NPs and/or nanostructures to add a “dock” onto each particle, to which biological molecules can attach subsequently. Thiol-containing compounds are widely used for Au particle modification, to utilize the easily formed S-Au bond. After the thiol ends of the molecules are anchored onto the Au particle surface, the chemical groups at the other end (i.e., $-\text{COOH}$ and $-\text{NH}_2$) can be made to react with the functional molecules (i.e., the antibody).

Thiolated polyethylene glycol (PEG) has been used to replace CTAB on Au nanorods. Small thiol-containing molecules, such as 3-amino-5-mercapto-1,2,4-triazole (AMTAZ), and 11-mercaptoundecaonic acid (MUDA), have also been used to modify Au nanorods, and subsequent attachment of antibodies were demonstrated (Yu et al. 2007a,b). In this approach, the Au nanorods were kept at an elevated temperature, to facilitate CTAB removal, and subjected to

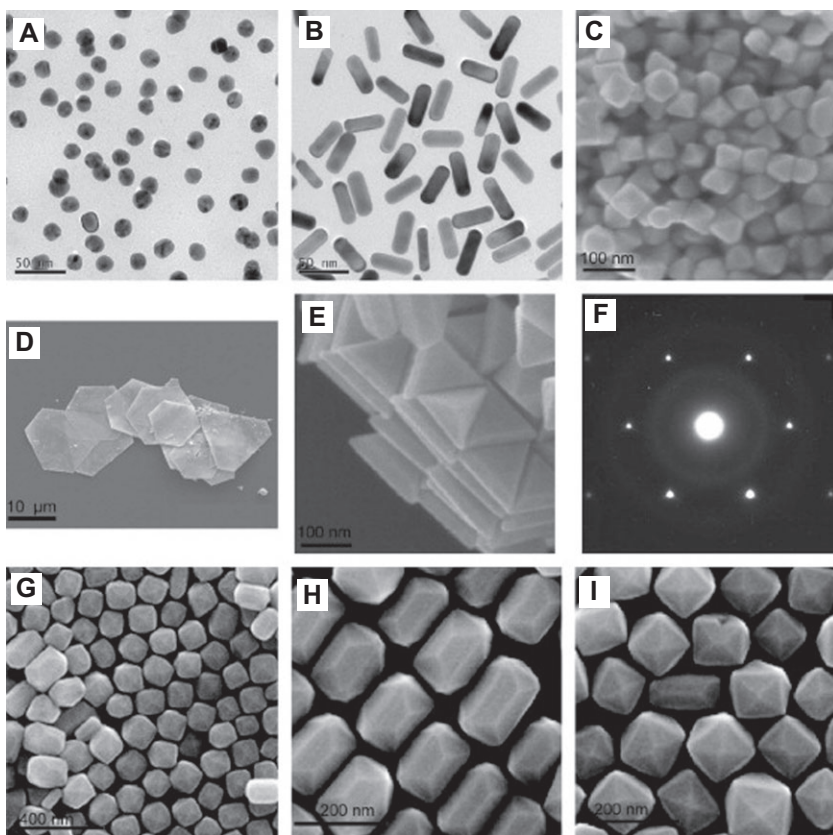


Figure 2 (A) TEM images of spherical gold nanoparticles (AuNPs) and (B) gold nanorods, (C) SEM image of gold nano-octahedra, (D) hexagonal nanoplates with an average lateral size of 7 nm, (E) SEM image of the gold nanoprisms with a three-dimensional (3D) pattern, (F) selected area (electron) diffraction (SAED) pattern taken from a single nanoprism, (G) SEM image of the tetrahexahedra AuNPs deposited on a Si substrate and (H) and (I) SEM images showing their side and end facets, respectively (Wang et al. 2010). Copyright Elsevier B.V. and reproduced with permission.

constant sonication to minimize particle aggregation. The general scheme to make molecular probes using AuNPs is illustrated in Figure 3.

In a recent approach, Hamad-Schifferli and coworkers developed a round-trip modification process to replace CTAB on Au nanorods with mercaptohexanoic acid (MHA) and then attached single-strand DNA to them (Wijaya and Hamad-Schifferli 2008, Wijaya et al. 2009). In this process, CTAB-coated Au nanorods were firstly subjected to an aqueous-to-organic phase transfer, in which CTAB was replaced by dodecanethiol (DDT). Then, an organic-to-aqueous phase transfer was performed, in which DDT was replaced by MHA, resulting in an MHA-coated Au nanorods aqueous solution. Finally, thiolated single-strand DNA was attached to the Au nanorods through further ligand exchange with MHA (Wijaya and Hamad-Schifferli 2008, Wijaya et al. 2009). In any functionalization efforts with DNA and DNA hybridization, charge screening (salt-aging) was necessary to compensate for the electrostatic repulsion between the negatively charged DNA molecules (Hill and Mirkin 2006).

Application of AuNPs in detection of chemical pollutants in water

Potential applications of AuNP probes in environmental analysis include chemical sensing and imaging

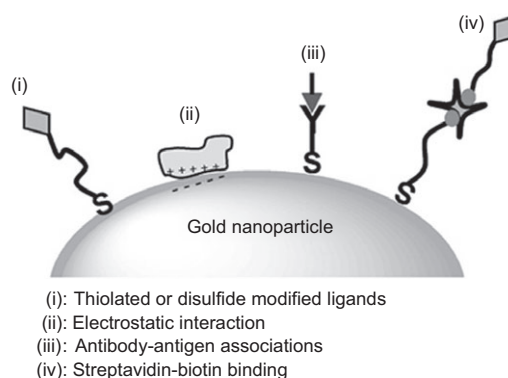


Figure 3 Schematic representation of formation of gold nanoparticle probes (Wang and Ma 2009). Copyright Elsevier B.V. and reproduced with permission.

applications. The color changes associated with NP aggregation, and/or local refractive index change, have been exploited as optical sensing methods for the detection of toxins (Wang et al. 2007, Liu et al. 2008, Shim et al. 2009), heavy metals (Darbha et al. 2008, Xue et al. 2008, Li et al. 2009) and other environmental pollutants (Daniel et al. 2009, Dasary et al. 2009) in water, soil and other environmental samples.

AuNPs are also being used to enhance the performance of electrochemical sensors due to their catalytic properties (Rassaei et al. 2011). Electrochemical sensors have been widely investigated for use in environmental pollutants screens. Generally, in these approaches, electrodes are first modified with AuNPs to increase their surface area for analyte absorption and catalytic reduction of the analytes, to generate the electrical readout signals (Rassaei et al. 2011). The AuNPs can also be functionalized with molecular capturing agents (i.e., antibodies, oligonucleotides, small molecules) to interact specifically with their molecular targets. Highly sensitive yet very rapid detection of various toxins and pollutants in water has been reported (Gooding et al. 2009, Zhang et al. 2010). In general, Au-NP-based sensing technology provides a useful platform for the detection of a wide range of toxins and pollutants (as shown in Table 1), and could

be extended toward the onsite monitoring of the hazard components in environmental matrices, including water (Wang et al. 2010).

Here, we provide an overview of recent examples of AuNP probe-based and/or AuNP-assisted assays involved in the detection of: (1) heavy metal cations; (2) aromatic compounds; (3) inorganic pollutants; (4) organophosphate; and (5) toxins.

Heavy metal cations

Heavy metal cations such as Pb^{2+} , Cu^{2+} , Cr^{2+} and Hg^{2+} are the commonly encountered toxic substances in the environment and pose significant public health hazards when they are present in drinking water, even in parts per million concentrations (Lewism and Cohen 2004, <http://www.epa.gov/mercury/about.htm>). In particular, Pb^{2+} is dangerous for children, causing mental retardation (<http://www.epa.gov/mercury/about.htm>). Colorimetric sensors using AuNPs have been widely explored and have important applications in the sensitive detection of metallic ions (Liu and Lu 2003, 2007, Lu and Liu 2007, Nakashima et al. 2007, Yoosaf et al. 2007, Li et al. 2008). Through a clever design of a DNzyme,

Detection target	Sensor type	Sensitivity	Reference
Heavy metal cations			
Pb^{2+}	Colorimetric sensor	3 nM	Liu and Lu 2007
Hg^{2+}	Cation-specific functionalized sensor	0.2 ppb	Lee et al. 2007
Divalent heavy metal ions	Direct electrostatic aggregation sensor	nM	Kim et al. 2001
Cu^{2+}	Electrochemical sensor	<1 μM	Gooding et al. 2009
Aromatic compounds			
2,4,6-trinitrotoluene (TNT)	Cysteine-modified AuNP-based label-free sensor	2 μM	Dasary et al. 2009
Nitrobenzene	Electrochemical sensor	0.3 mg/l	Liu et al. 2006
Inorganic pollutants			
Nitrite ions	Crosslinking colorimetric sensor	Sub-ppm	Daniel et al. 2009
Nitrite ions	Non-crosslinking colorimetric sensor	<1 ppm	Xiao and Yu 2010
Nitrite ions	Electrochemical sensor	0.1 μM	Zhang and Yi 2009
Hypochlorite	Electrochemical sensor	1 μM	Tsai et al. 2011
Arsenic	Electrochemical sensor	30 ppb	Rassaei et al. 2008
Organophosphate			
Organophosphates and phosphonates (OPPs)	Optical sensor	0.5 μM	Newman et al. 2007
OPP compounds/pesticides	Electrochemical sensor	0.1 nM	Chauhan et al. 2011
Toxins			
Ricin	AuNPs conjuncted with lateral flow strip assay	10 pg/ml	Uzawa et al. 2008
Ochratoxin A (OTA), zearalenone (ZEA), aflatoxin B1	Immunochromatographic strip assay	0.32 ng/ml, 2.5 ng/ml	Bo et al. 2007, Liu et al. 2008, Shim et al. 2009

Table 1 Summary of the detection sensitivity achieved by gold nanoparticle-based sensor platform.

which will be activated by the presence of Pb^{2+} , a colorimetric assay has been developed by Lu and coworkers (Liu and Lu 2003, 2007, Lu and Liu 2007). In this scheme, as shown in Figure 4, the presence of Pb^{2+} in water will activate the DNAzyme and cause cleavage of the DNA crosslinks between the inter-connected AuNP aggregates. The disintegration of the aggregates leads to a colorimetric change that can be easily monitored, which in turn indicates the presence of the Pb^{2+} in the water sample. The AuNP-based colorimetric assay does not utilize organic co-solvents, enzymatic reactions, light-sensitive dye molecules, lengthy protocols, or sophisticated instrumentation, thereby overcoming some of the limitations of the more conventional methods. The sensitivity of this colorimetric scheme is 3 nM for Pb^{2+} , much lower than the Environmental Protection Agency standard for drinking water (Liu and Lu 2007, Lu and Liu 2007). In particular, the dynamic range of Lu's sensor can be tuned simply by adjusting the pH (Lu and Liu 2007).

Cation-specific functionalized AuNPs have also been developed for the detection of Hg^{2+} (Liu and Lu 2003, Lin et al. 2006, Nakashima et al. 2007, Li et al. 2008). A substantial improvement in the sensitivity (1 nM, 0.2 ppb) over conventional methods was achieved. Based on the Hg^{2+} -mediated formation of T-Hg²⁺-T base pairs, a highly sensitive and selective Hg^{2+} detection assay has also been developed by Xue et al. (2008) and Lee et al. (2007). This is based on Hg^{2+} induced thymine-thymine (T-T) mismatches in DNA-modified AuNPs to form particle aggregates

at room temperature, with a concomitant colorimetric response. This method is enzyme free and does not require specialized equipment, other than a temperature control unit. The concentration of Hg^{2+} can be determined by the change of the solution color at a given temperature, or the melting temperature (T_m) of the DNA-AuNP aggregates. Significantly, this method can, in principle, be used to detect other metal ions, by substituting the thymidine in the study with synthetic artificial bases that selectively bind other metal ions. To overcome some drawbacks [e.g., the high cost of tags (DNAs or fluorescent dyes) and shelf-life of the sensors] of colorimetric assays, recently, Darbha and co-workers demonstrated that second order non-linear optical (NLO) properties of AuNPs can be used for screening mercury from environmental samples, without any DNA or fluorescent tag, with excellent sensitivity (5 ppb) and selectivity (Darbha et al. 2008).

Direct electrostatic aggregation of AuNPs has also been explored for the rapid detection of heavy metal ions. Kim and coworkers (Kim et al. 2001) designed a simple scheme (Figure 5A) in which the ion templated chelation of AuNPs leads to a rapid colorimetric response, through which the presence of divalent heavy metal ions (Pb^{2+} , Cd^{2+} , Hg^{2+}) can be determined.

In a different, electrochemical sensing approach, Gooding and coworkers (Gooding et al. 2009) developed an electrochemical sensor for copper ions that has a limit of detection below 1 pM. Electrodes were first modified with AuNPs, and then the gold colloid surface was modified with cysteine for copper detection.

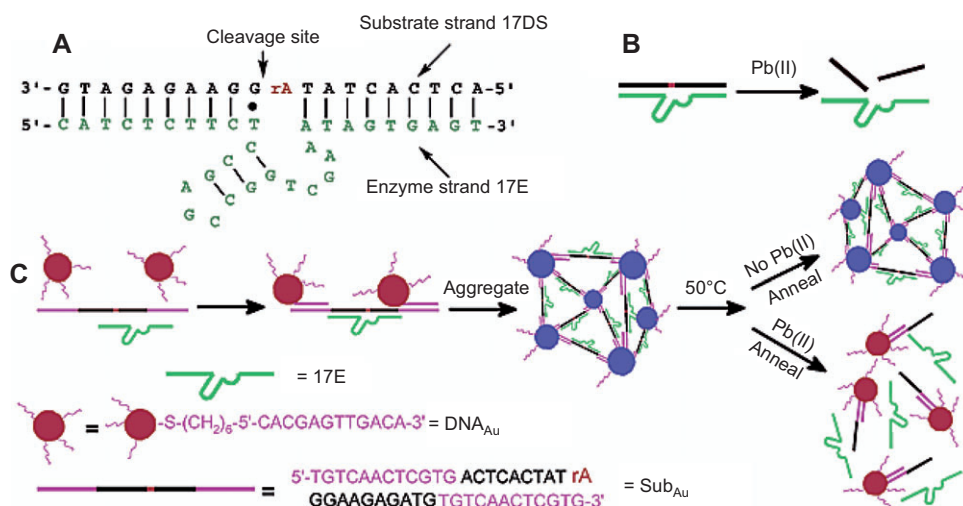


Figure 4 (A) The secondary structure of the “8–17” DNAzyme, which consists of an enzyme strand (17E) and a substrate strand (17DS). The cleavage site is indicated by a black arrow. Except for a ribonucleoside adenosine at the cleavage site (rA), all other nucleosides are deoxyribonucleosides. (B) The cleavage of 17DS by 17E in the presence of Pb^{2+} , (C) schematics of DNAzyme-directed assembly of Au nanoparticles and their application as biosensors for metal ions such as Pb^{2+} . In this system, the 17DS has been extended on both the 3' and 5' ends for 12 bases, which are complementary to the 12-mer DNA attached to the 13-nm Au nanoparticles (DNA^{Au}) (Liu and Lu 2003). Copyright American Chemical Society and reproduced with permission.

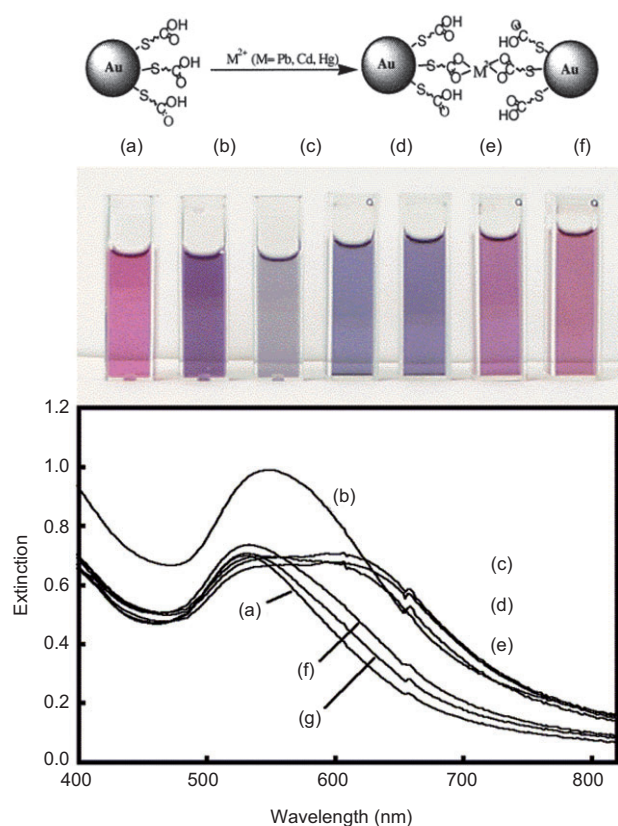


Figure 5 Colorimetric detection for divalent heavy metal ions (top panel: mechanism scheme) and corresponding colorimetric and spectral traces (bottom panel) from: (a) gold particles capped with 11-mercaptopundecanoic acid (Au-MUA), (b) Au-MUA/Pb²⁺ and (c) to (g) Au-MUA/Pb²⁺ and increasing amounts of EDTA. The Pb²⁺ concentration in sample (b) is 0.67 mM; EDTA concentrations in samples (c) to (g) are 0.191, 0.284, 0.376, 0.467, and 0.556 mM, respectively, (Kim et al. 2001). Copyright American Chemical Society and reproduced with permission.

Aromatic compounds

Aromatic compounds are important industrial chemicals, widely used in the pharmaceutical, plastic, dyes, rubber, and pesticide industries. When they are being discharged in waste water, they usually can find their way to soil and water supplies, and pollute the environment. Even at low concentrations, aromatic compounds can pose high risks to public health (Khadikar et al. 2002, Bhatkhande et al. 2003).

Traditionally aromatic compounds are detected and characterized by HPLC-based chromatographic methods, which are time consuming and labor intensive. In recent years, AuNP-based molecular probing techniques have been developed for the detection of aromatic compounds. Dasary et al. (2009) developed a cysteine-modified AuNP-based label-free surface-enhanced Raman spectroscopic probing method for the detection of trace amounts of

2,4,6-trinitrotoluene (TNT) (with a detection limit of 2 pM) in aqueous solution. TNT is the most commonly used nitroaromatic explosive; its contamination of soil and ground water is a major concern in war-torn countries in the Balkans, Africa and the Middle East. In Dasary's approach, AuNPs were functionalized with cysteine, which reacts with TNT to cause aggregation of the AuNPs in the presence of TNT. The subsequent color change of the AuNP suspension, and further SERS spectroscopic characterization of the TNTs, confirmed the detection of TNTs.

AuNPs have also been utilized to improve the sensitivity of electrochemical detection of aromatic compounds. A recent trend is to attach AuNPs to the surface of multi-wall carbon nanotubes (MWNTs) and/or single-wall carbon nanotubes (SWNTs), to create highly sensitive electrodes that can capture small voltammogram changes associated with the reduction of the analytes in contact with the electrodes (Liu et al. 2006). With this approach, Liu and coworkers demonstrated the detection of nitrobenzene in water, with a LOD of 0.3 mg l⁻¹.

Inorganic pollutants

AuNPs have also been widely used in sensing applications for a variety of inorganic pollutants. Nitrate and nitrite, as part of the nitrogen cycle, widely exist in ground and surface water systems, due to contaminations of water sources by fertilizer, waste of livestock and other organic wastes (USEPA 1995, Nollert 2000). Even trace amounts of nitrate and nitrite ions are unsafe to human health, and both are type A inorganic chemicals in water quality parameters which require close monitoring by health authorities, due to their potential toxicity (Zuane 1996). Conventional methods for nitrite/nitrate detection require sophisticated instrumentation and are not suitable for deployment in the field. An AuNP-based colorimetric assay offers an easy-to-use solution for nitrite/nitrate detection with high sensitivity. Daniel and coworkers developed a crosslinking colorimetric method, in which nitrite ions serve as crosslinking bridges to inter-connect AuNPs to trigger colorimetric responses at sub-ppm levels based on AuNPs, to detect low levels of nitrite ions (Daniel et al. 2009). More recently, our lab developed a non-crosslinking colorimetric assay for nitrite (Xiao and Yu 2010). In this approach, 4-aminothiophenol (4-ATP) modified gold nanorods (GNR) were utilized as nitrite sensors. In the presence of nitrite, a deamination reaction was induced by heating the 4-ATP modified GNR in ethanol solution.

This resulted in the reduction of the GNR surface charges, which led to aggregation of GNRs and a colorimetric response that was quantitatively correlated to the concentration of nitrite ions. As shown in Figure 6, the critical coagulation concentration (CCC) of nitrite, which is the concentration of the nitrite in the sample that will trigger the colorimetric change of the GUR probes, is quantitatively correlated to the heating time. Simply by measuring the heating time needed for the color change to develop, a rapid (≤ 10 min) and highly sensitive (< 1 ppm of nitrite) assay of nitrite can be achieved, that potentially can be used for rapid monitoring of water quality. With the addition of enzymatic reactions to reduce nitrate to nitrite, these approaches can easily be implemented for nitrate detection as well (Daniel et al. 2009, Xiao and Yu 2010). AuNP assisted electrochemical sensors have also been developed to detect nitrite (Li 2009, Liu et al. 2009, Zhang and Yi 2009). Generally, AuNPs are deposited on glassy carbon electrodes, and the excellent catalytic activity of the AuNPs towards the oxidation of nitrite is utilized to detect nitrites with cyclic voltammetry at $\sim 10^{-7}$ M, without any major interference. In a recent report (Tsai et al. 2011), AuNPs were incorporated into a poly (3,4-ethylenedioxythiophene) film on the surface of electrodes, to create an electrochemical sensor for the detection of hypochlorite, another inorganic pollutant, in water at 1 μM level.

Another important inorganic pollutant for water is arsenic. Au is known to be the most appropriate material to measure arsenic in an electrochemical sensing setup, but the analysis of arsenic by the anodic stripping voltammetry (ASV) method is limited by the formation of a monolayer of AsO deposition, due to the non-

conductive property of the As-Au compound. AuNPs with a large surface area have been used to overcome this limitation in many studies, but their performance depends on their size, shape and distribution during the nucleation process, which is followed by particle growth (Dai and Compton 2006, Rassaei et al. 2008). Further investigation is still needed to optimize the sensitivity of the detection.

Organophosphate

Over the past several years, organophosphates and phosphonates (OPPs) have become increasingly important as analytes for water quality evaluation. Many nerve agents and pesticides are organophosphates or organophosphonates, making the ability to detect small quantities or low concentrations of these compounds critically important. The ratification of the Chemical Warfare Convention has underscored the need to develop rapid, sensitive, and selective detectors for chemical warfare agents and other organophosphate/phosphonate compounds, in order to verify compliance with the provisions of the treaty (OPCW 2005). Contamination of groundwater and agricultural products entering the human food chain by organophosphate/phosphonate pesticides, has also led to the need for sensitive detection methods (Janotta et al. 2003, Halámek et al. 2005, Simonian et al. 2005, Liu and Lin 2006, Wang et al. 2006). AuNPs, as a surface area enhancing scaffold and a foundation for surface modification chemistry, have been utilized to create high-affinity material that is selective primarily for OPP compounds (Shipway

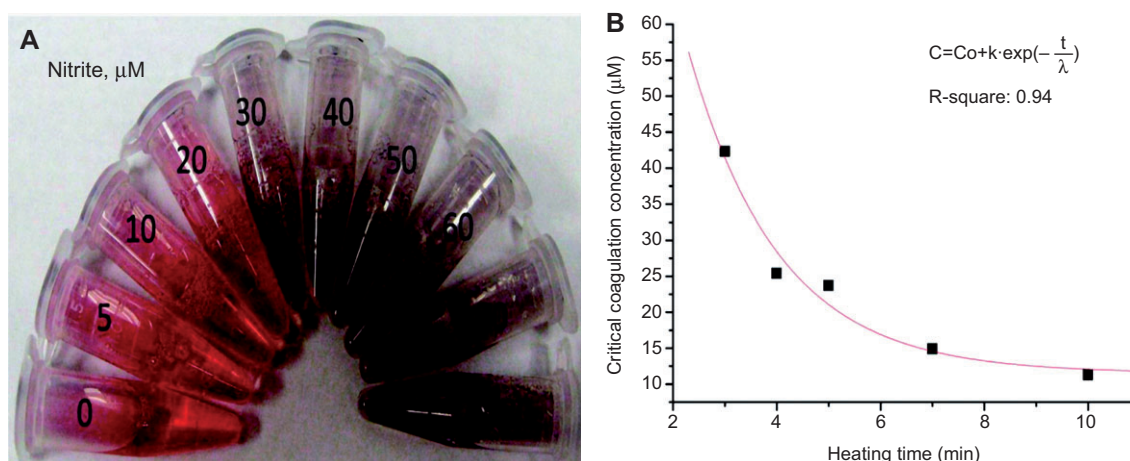


Figure 6 Colorimetric assay of nitrite in water using gold nanorods molecular probes. (A) Photograph of GNR-4ATP reacted with various concentrations of nitrite after incubation in 20% ethanol at 95°C, (B) critical coagulation concentration (CCC) of GNR-4ATP as a function of heating time (Xiao and Yu 2010). Copyright American Chemical Society and reproduced with permission.

et al. 2000, Chen and Katz 2002). Once the analytes have been absorbed onto this novel material, the SPR from the AuNPs can be monitored, with a relatively high signal-to-noise ratio, depending on the choice of solvent. With this approach, Newman et al. demonstrated a rapid detection of organophosphate at μM concentrations. As shown in Figure 7, the blue-shift of the SPR peak of AuNPs, upon absorption of OPPs, indicated the presence of OPPs in the samples (Newman et al. 2007).

In a more recent work, AuNP- CaCO_3 hybrid material was conjugated with acetylcholinesterase (AChE), and mounted onto gold electrodes, to serve as electrochemical sensors for the detection of organophosphate pesticides in water. The biosensor was based on the inhibition of AChE by OPP compounds/pesticides. Detection of OPP compounds down to 0.1 nM can be achieved in 10 min (Chauhan et al. 2011).

Toxins

Naturally occurring toxins, such as ochratoxin A (OTA), zearalenone (ZEA), aflatoxin B1, microcystin LR and others, originate from *Aspergillus ochraceus*, *Aspergillus flavus*, *Aspergillus parasiticus*, *Fusarium graminearum*, etc. They are found in cereals, cereal products, and coffee beans, and are considered to be teratogenic, mutagenic, and immunosuppressive to animals and humans (Wang et al. 2010). Another class of toxins, originating from *Bacillus botulinus*, *Escherichia coli*, or *Ricinus*

communis, is found in animal tissues and plants, which can induce targeted damage to the human body (Wang et al. 2010). All of these toxins may escape into agricultural run-off water and waste water from food processing facilities, and pose as public health threats. AuNP-based molecular probes have been developed in conjunction with a lateral flow strip assay, as a detection platform for monitoring the contamination of water by various toxins. Uzawa et al. (2008) utilized the naturally occurring infection mechanism and the strong affinity of the toxin ricin to sugar, to develop sugar-coated AuNPs for the detection of ricin with visual read-out. Immunochromatographic strip assays combine chromatography technology with conventional immunoassays, to provide a simple, low-cost and rapid tool for toxins diagnosis, with the aggregation of AuNPs as the colorimetric readout mechanism (Figure 8). Recently, many kinds of immunochromatographic assays, using AuNP-antibody conjugates, have been developed for the detection of OTA (Wang et al. 2007, Liu et al. 2008),

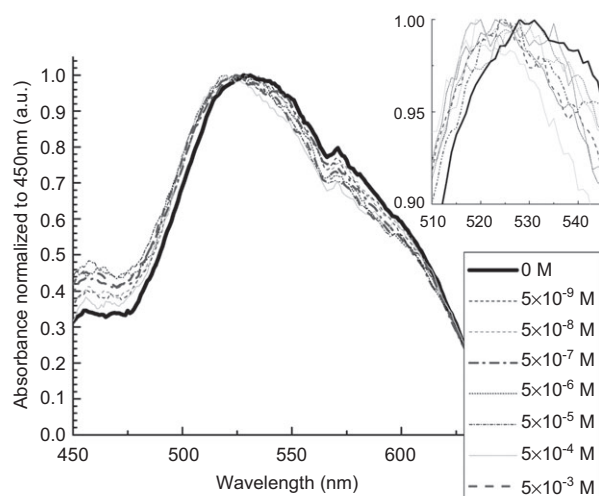


Figure 7 UV-visible spectra of silica gel sensor exposed to varying concentrations of diethyl chlorophosphate (DECP); the blue-shift of the SPR peak indicates the absorption of DECPs to the AuNP surfaces. Absorbance has been normalized to 450 nm absorbance (Newman et al. 2007). Copyright American Chemical Society and reproduced with permission.

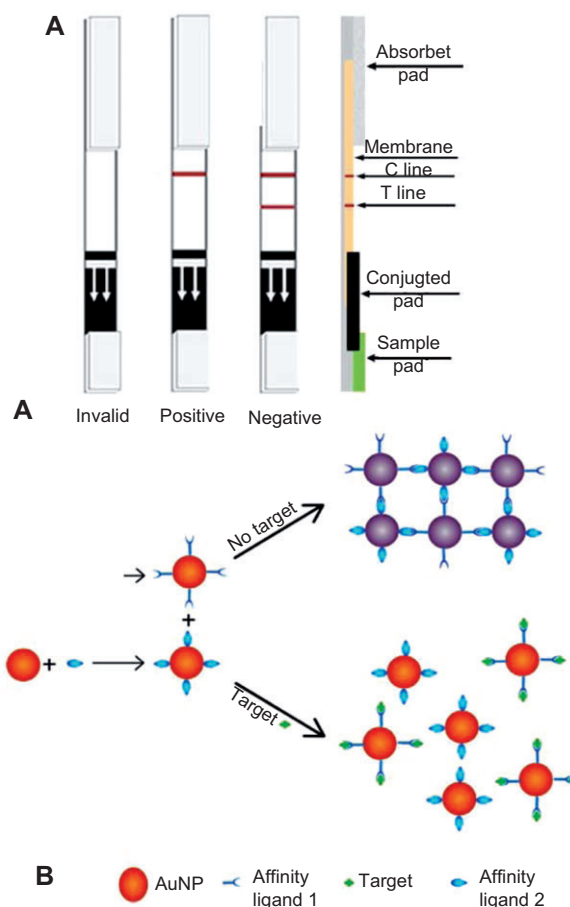


Figure 8 The schematic illustration of the immunochromatographic strip assay to evaluate toxin contamination in water samples. (A) Scheme of the strip assay and (B) the mechanism of gold nanoparticle (AuNP)-aggregation based colorimetric assay (Wang et al. 2010). Copyright Elsevier B.V. and reproduced with permission.

ZEА (Shim et al. 2009), and AFB1 (Bo et al. 2007). The immunochromatographic strip assay has the advantage of an easy operation format, a short assay time and stability over a wide range of conditions, which makes this technique useful for on-site testing by untrained analysts.

Conclusions and future perspectives

Environmental sensor research generates considerable interest and activity nowadays. In this review, we summarized the recent progress in AuNP synthesis, as applied to environmental sensing, and the use of AuNPs in the detection of environmental pollutants.

Over the past decade, advances in AuNP synthesis and fabrication have led to an explosion of both efforts and reports on the emerging field of AuNP-plasmonics. Significant progress has been made in creating novel nano-sized sensors for chemical and biological sensing and imaging. AuNP-based sensors provide promising approaches for selective and sensitive analyses, and have advantages over traditional instrumental analyses, as they are usually compatible with portable devices that can be deployed in field for onsite sample screening. With the advance of microfluidic sample handling units, this kind of portable device can be developed for multiplexed, quantitative and rapid analysis, and can measure unprocessed field-collected water samples with a high sensitivity. High-throughput and ultrasensitive detection technology, based on AuNPs, offer effective screening

methods for many environmental analytes. This technology will certainly find widespread applications in water quality and safety monitoring in the near future.

Researchers worldwide are actively exploring two lines of researches: (1) new materials, such as anisotropic-shaped AuNPs, or Au alloy NPs, are being fabricated and new theories and models are being developed and investigated to expand our understanding of plasmonic phenomena at the nanoscale; and (2) new sensing instruments and/or platforms are being designed and exploited, based on the growing knowledge bases, to provide unprecedented sensitivity and resolution for chemical and biological sensing and imaging. These two lines of research are merging to yield next-generation nanosensors. However, it should be noted that a number of critical issues still need to be addressed before they can become realistic tools for environmental monitoring. Reliable manufacturing methods to produce AuNPs in a large scale, with good reproducibility, are still lacking, especially for anisotropic shaped particles; long-term health effects of nanomaterials still need to be characterized and a high throughput assay, which is very important for environmental applications, needs to be developed in field-deployable platforms. Nevertheless, we expect, in the near future, that increased collaboration between scientists from different disciplines will yield new fundamental insights into the AuNP-based nanotechnology and result in more powerful nanosensors for various applications.

Received June 24, 2012; accepted September 12, 2012; previously published online November 9, 2012

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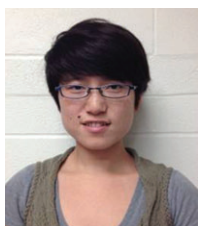
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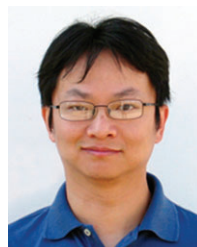
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