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# Portable and smart devices for monitoring heavy metal ions integrated with nanomaterials

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With increasing concerns of ecological environment, safe drinkable water and healthy food, the detection for heavy metal ions (HMIs) becomes an attractive research field. On the basis of optical, electrical and other signals from nanomaterials, many interesting methods and portable devices for detection of HMIs are growing flourishingly. In this review, we focus on the portable and smart devices integrated with nanomaterials for monitoring HMIs. The interesting design of the miniaturization, portability, and commercialization of HMIs detection devices are summarized and introduced comprehensively.



## 1. Introduction

Rapid growth of global economy and industry has caused increased environmental concerns recently. Heavy metal ions (HMIs) are one kind of the most problematic pollutants because they are non-biodegradable and can enrich in ecological systems easily. In daily life activities, some HMIs play important biochemical functions with trace amounts. While, high concentrations of heavy metal ions are toxic to the metabolic process and have threat to some organisms. For instance, copper is a necessary element for the human body utilized in many life activities, however, unregulated copper ion ($Cu^{2+}$) can cause a series of diseases, such as Alzheimer, Parkinson, anemia and arteriosclerosis [1]. Lead ion ($Pb^{2+}$), mercury ion ($Hg^{2+}$), cadmium ion ($Cd^{2+}$) and other high poisonous ions which get excreted very slowly in human body can seriously affect the function of the cardiovascular system, kidneys, lungs, bones, nervous tissues and the immune system [1,2]. Therefore, detection of heavy metal ions, especially in drinkable water and food is extremely important.

Several instrumental analysis technologies are developed for the detection of HMIs, including inductively coupled plasma mass spectrometry (ICP–MS), inductively coupled plasma–atomic/optical emission spectrometry (ICP–AES/OES), flame atomic absorption spectrometry (FAAS), and atomic absorption spectrophotometry (AAS) [3,4]. The instrumental measurements for HMIs have some obvious advantages, such as high sensitivity, selectivity, and accuracy. However, the instrumental analysis is associated with shortcomings of long pre-concentration steps, professional operations, complex and costly instrumentations, which limit the detection of HMIs out of lab. Meanwhile, miniaturized and portable devices for monitoring HMIs are required urgently for application in on-site detection.

Nanomaterials have been already studied in optical and electrochemical sensors for many analytes due to their excellent optical, electrical, catalytic properties on the basis of their quantum size effects. Multiple surface modification, assembly process and big surface area give the nanoprobes more advantages in high sensitivity, good selectivity and fast response. Compared with conventional organic probes and traditional sensors, nanomaterials can be applied for trace detection, complex sample analysis, and multi-components assays. Generally, the simple operation, cost-effective and portable detection devices yield worse sensitivity and selectivity due to the size limitation of the devices. The application of nanoprobes can cover the shortage of a portable device and shows a good sensitivity and selectivity. So, the convenient and portable devices based on nanomaterials are highly demanded and the portable devices integrated with nanoprobes is a good choice for monitoring HMIs in the samples.

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The modules of the ion detection system include target recognition unit, signal generation unit, signal transduction or amplification unit, signal reception unit and signal processing unit (Fig. 1). Many materials and devices have been designed to miniaturize the different moieties of the ion detection system. Generally, nanotechnology can integrate and miniaturize the first three units successfully by exploration of novel functional nanomaterials, such as gold nanoparticle, quantum dot, graphene, polymer nanofiber, and so on. Microfluidic device can realize the separation of targets in a complex sample and integrate analysis process on a piece of chip. Mobile phone, photometer, intelligence chip and other smart devices are used to replace the traditional signal detector and workstation. The integration of the nanomaterials and these convenient instruments can explore various kinds of small, portable, convenient detection units, and be used in HMIs detection.

Many review articles have been published to exclusively focus on the functional nanomaterials and sensors in HMIs detection [5–12]. With the development of portable and smart detection device researches, the main aim of this mini review is to highlight some of the recent advancements of the novel detection methods and portable, smart HMIs detection devices with different signal categories (Fig. 2). The convenient HMIs devices are more helpful in environmental monitoring, food safety and other industrial fields.

## 2. Optical signal detection devices

### 2.1. Optical nanoprobes

Optical sensors can detect the presence of HMIs in aqueous solution through optical signals including optic absorption, reflection, scattering, and emission. Gold nanoparticles (AuNPs), quantum dots (QDs), upconversion nanoparticles (UCNPs) and other functional nanomaterials have been used in HMIs detection successfully. Because of their special optical properties, the nanomaterial probe acts as an important optical-translating unit and signal amplification unit in the construction of optical sensors.

Colorimetric assay is based on color change which can be recognized by human eyes directly. Many colorimetric assays applying nanomaterials are used in HMIs detection in recent years. Generally, the optical properties can be tuned via target-induced aggregation/anti-aggregation or the surface states change of nanomaterials. Combining with the specific recognition unit, such as small molecular ligands, functional macromolecules, oligonucleotides and specific chemical/biological reactions, the nanomaterial-based optical sensors can show the specific and selective response to the target molecules [8]. The response to the target induces changes of the aggregation state and the energy transfer of nanomaterials and monitors the target. The most representative examples are gold and silver nanoparticle sensors. The excellent longitudinal surface plasmon resonance (LSPR) properties of gold and silver nanoparticles strongly dependent on the interparticle distance. The decrease of the distance between nanoparticles can trigger the coupling of interparticle surface plasmon, which induce a red shift in the LSPR band and a visual color change, from red to blue for gold nanoparticles (AuNPs) and yellow to brown for silver nanoparticles (AgNPs) [8]. The color change mediated by interparticle distance provides a series of strategies for colorimetric sensing of HMIs. The core design principle is to modify gold or silver nanoparticles with functional ligands for recognizing targets, and triggering the change of interparticle distance of nanoparticles. For instance, glutathione and cysteine are widely used to decorate AuNPs to detect many HMIs like $Hg^{2+}$, $As^{3+}$, $Pb^{2+}$, $Cd^{2+}$. These ligands contain amino or carboxy groups to recognize HMIs and change interparticle distance via ligand–HMIs coordination [13]. DNA is another most used ligand for AuNPs decoration to detect HMIs through two mismatch base forming base–HMIs–base complex, such as thymine–$Hg^{2+}$–thymine (T–$Hg^{2+}$–T) and cytosine–$Ag^{+}$–cytosine (C–$Ag^{+}$–C) [14]. And the facile bare AuNPs can be synthesized and succeeded in the colorimetric sensor selectivity detecting $Cr^{3+}$ ions [15]. Synergistic catalytic effect of nanomaterials can be applied in HMIs detection either. Recently, the gold nanoclusters (AuNCs) catalyst colorimetric system of 3,3′,5,5′-tetramethylbenzidine (TMB) and $H_2O_2$ to detect $Hg^{2+}$ is proposed [16]. AuNCs can catalyze the reduction of $Hg^{2+}$ implying amalgam formation which amplify the catalytic activity on TMB–$H_2O_2$ reaction system and make color change of TMB from colorless to dark blue.

Although colorimetric assays based on SPR nanoprobes can simplify the detector, the detection progress happens in solution, which hinders the on-site detection, quick analysis and other practical application of colorimetric in detection of HMIs. To realize smart and portable devices in HMIs detection, transforming liquid platform into solid platform is an effective strategy to simplify the detection operation, such as papers, strips, integrated chips, and so on.

### 2.2. Paper and strip devices

Cooperating nanomaterials with test paper makes colorimetric more rapid, sensitive, selective, and user friendly. The nanomaterials for sensing HMIs like AuNPs are riveted on paper or other

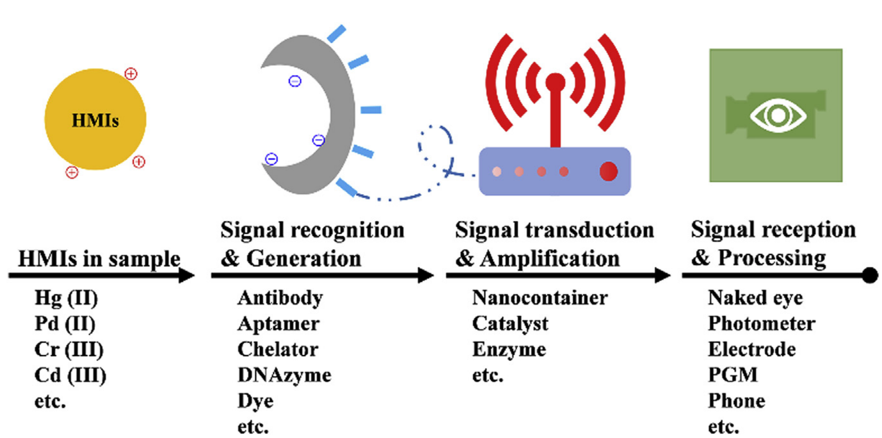


**Fig. 1.** The HMIs detection system contains sample, recognition & signal generation unit, signal transduction & amplification unit and signal reception & processing unit. Each part of the HMIs detection system can be designed to small and smart device component by nanotechnology and novel design.