Determination of mercury (II) ions based on silver-nanoparticles-assisted growth of gold nanostructures: UV–Vis and surface enhanced Raman scattering approaches

Jun-Liang Chen [a], Pei-Chia Yang [a], Tsunghsueh Wu [b,*], Yang-Wei Lin [a,*]

[a] Department of Chemistry, National Changhua University of Education, 1 Jin-De road, Changhua City, Changhua County 500, Taiwan
[b] Department of Chemistry, University of Wisconsin-Platteville, 1 University Plaza, Platteville, WI 53818-3099, USA

ABSTRACT

Innovative dual detection methods for mercury(II) ions ($Hg^{(II)}$) have been developed based on the formation of gold nanostructures (AuNSs) following the addition of mercury-containing solution to a mixture containing an optimized amount of $Au^{(III)}$, H_2O_2, HCl, and silver nanoparticles (AgNPs). In the absence of $Hg^{(II)}$, the addition of $Au^{(III)}$, H_2O_2, and HCl to the AgNP solution changes the solution's color from yellow to red, and the absorption peak shifts from 400 to 526 nm, indicating the dissolution of AgNPs and the formation of gold nanoparticles (AuNPs). Because of the spontaneous redox reaction of $Hg^{(II)}$ toward AgNPs, the change in the amount of remaining AgNP seed facilitates the generation of irregular AuNSs, resulting in changes in absorption intensity and shifting the peak within the range from 526 to 562 nm depending on the concentration of $Hg^{(II)}$. Under optimal conditions, the limit of detection (LOD) for $Hg^{(II)}$ at a signal-to-noise ratio (S/N) of 3 was 0.3 μM. We further observed that AgNP-assisted catalytic formation of Au nanomaterials deposited on a surface enhanced Raman scattering active substrate significantly reduced the Raman signal of 4-mercaptobenzoic acid, dependent on the $Hg^{(II)}$ concentration. A linear relationship was observed in the range 0.1 nM–100 μM with a LOD of 0.05 nM (S/N 3.0). As a simple, accurate and precise method, this SERS-based assay has demonstrated its success in determining levels of $Hg^{(II)}$ in real water samples.

Published by Elsevier B.V.

1. Introduction

Monitoring the level of mercury (II) ions ($Hg^{(II)}$) present in aquatic ecosystems is important, first because $Hg^{(II)}$ poses a serious threat to aquatic life, and second because by accumulating in aquatic species in the food chain, $Hg^{(II)}$ causes harmful effects to humans [1,2]. Exposure to $Hg^{(II)}$ results in irreversible impairments to the brain and the nervous system, causing symptoms such as tremors, vision problems, deafness and loss of muscle coordination, sensation, and memory [3]. To protect human health, the United States Environmental Protection Agency (US EPA) has set the maximum level of mercury in drinking water and polluted industrial wastewater to be 10 nM (2.0 ppb) and 250 nM (50.0 ppb), respectively [4]. Several quantitative techniques, such as flame atomic absorption spectrometry, inductively coupled plasma mass spectrometry, and selective cold vapor atomic fluorescence spectrometry [5–11], have been applied for $Hg^{(II)}$ detection in environmental samples; however, these methods require bulky, expensive instruments and tedious sample preparation procedures, limiting their applicability to on-site $Hg^{(II)}$ analysis. Therefore, developing rapid, sensitive, selective,

and portable analytical techniques with minimal sample treatment for determining $Hg^{(II)}$ concentrations would simplify environmental monitoring and enable fast responses to mercury-contaminated water.

Nanomaterials are popular in several fields because of their unique optical, electronic, magnetic, and catalytic properties, making them ideal candidates for signal generation and transduction in the detection of various analytes of interest. Gold nanoparticles (AuNPs) are the most commonly used optical sensing nanomaterials because of their strong surface plasmon resonance (SPR) absorption characteristics in the visible region, simple preparation, high stability, and biocompatibility [12–15]. The characteristics of SPR absorbance in AuNPs can be determined from their extinction coefficients, which can reach as high as 10^{10} M^{-1} cm^{-1} and are extremely sensitive to the chemical nature, size, and shape of the AuNPs, to their interparticle distance, and to the nature of the surrounding media. These fascinating optical properties enable AuNPs to function in niche sensing applications for the selective and sensitive detection of a wide range of potentially toxic metal ions (e.g., $Hg^{(II)}$, $Pb^{(II)}$, $Cu^{(II)}$) [16–20]. By taking advantage of the unique functional groups in organic molecules, their affinity to target metal ions, and agglomeration-induced changes in the optical properties of AuNPs, several organic molecules (such as Tween-20, 3-mercaptopropionic acid, 11-mercaptoundecanoic acid, glutathione,

* Corresponding authors.
   E-mail addresses: wut@uwplatt.edu, (T. Wu), linywjerry@cc.ncue.edu.tw. (Y.-W. Lin).

and polythymine oligonucleotides) have been used to modify AuNPs to improve the specificity in the detection of heavy metals [16,20]. However, the composition of the buffer solution in the detection method has a strong influence on the selectivity and sensitivity of these modified AuNP-based sensors for two reasons. First, the buffer solution controls the surface charge density of the AuNPs, determining the fate of AuNPs as uniformly suspended particles or coagulated nanoparticle clusters [21]. Second, the buffer species can form complexes with metal ions of interest, reducing the affinity to the sensing elements immobilized on the AuNP surfaces. Thus, fine control of the buffer composition and fine control of the ligand density on the AuNP surfaces are both required for obtaining reproducible results. Another drawback of sensing based on modified AuNPs is that surface modification caused by recognition of organic molecules often degrades the superior optical properties of the AuNPs. To overcome the drawbacks, a colorimetric detection of $Hg^{(II)}$ with good selectivity and sensitivity (50 nM) by using unmodified AuNPs was proposed by Chen's group [22]. A sensing scheme is based on only $Hg^{(II)}$ can prevent the aggregation of AuNPs induced by melamine. However, using melamine may produce other environmental pollutants. In addition to AuNPs, Rastogr et al. demonstrated a simple ligand-free colorimetric detection by using gum knodagogu reduced/stabilized silver nanoparticles (AgNPs) [23]. The limit of quantification for $Hg^{(II)}$ using the proposed method was as low as 50 nM. However, chemical reagent (gum kondagogu Grade 1) for the preparation of AgNPs could not be acquired easily. In 2012, Wang et al. proposed an ultrasensitive colorimetric detection of $Hg^{(II)}$ based on a catalytic reduction property of AgNPs [24]. The addition of H_2O_2 to the mixture of AgNPs and $Hg^{(II)}$ induced obvious color changes in the solution even at 2.0 nM $Hg^{(II)}$. Interestingly, Jarujamrus's results revealed a significant enhancement in the $Hg^{(II)}$ sensitivity when $Cu^{(II)}$ was doped onto unmodified AgNPs in the absence of H_2O_2, thereby improving the quantitative detection limit to 2.5 nM [25]. However, toxic $Cu^{(II)}$ ions were used, which caused another environmental problem. Recently, surface-enhanced Raman scattering (SERS) has become a promising alternative method for $Hg^{(II)}$ analysis [26,27]. Numerous methods for SERS detection of $Hg^{(II)}$ have been reported based on the "reporter approach" and "T–$Hg^{(II)}$–T approach" [26]. The first well-known Raman reporter approach was based on the specific interaction between $Hg^{(II)}$ and Raman reporters (Raman active molecules). The T–$Hg^{(II)}$–T approach relies on the thymidine–$Hg^{(II)}$–thymidine coordination chemistry. To the best of our knowledge, no study on determination of $Hg^{(II)}$ by using the catalytic reduction property of AgNPs combined with SERS detection has yet been published.

In this study, the serendipity of $Hg^{(II)}$ sensing was determined by using AgNP seed for the formation of gold nanostructures (AuNSs) in the presence of $Au^{(III)}$/HCl/H_2O_2. This mass of AgNP seed catalyzed the reduction reaction of $Au^{(III)}$ ions and produced an obvious color change in the AgNP solution. To understand the overall reaction and optimize the sensor performance, the effects of the reaction temperature, time, the concentrations of constituents, such as AgNP seed, $Au^{(III)}$, HCl, and H_2O_2, on the selectivity and sensitivity in the presence of $Hg^{(II)}$ were evaluated. To further improve the sensitivity, an SERS assay for sensing $Hg^{(II)}$ was investigated to determine the influence of the catalyzed products (AuNPs or AuNSs) on the SERS enhancements of the Ag microflower-like structures electrodeposited on screen-printed carbon electrode (AgMF-SPCE) substrates [28–30]. The developed SERS detection platform was then validated through the detection of $Hg^{(II)}$ in real water samples. Finally, this study explores a new prospect of utilizing the catalytic reduction property of AgNPs to develop both colorimetric and SERS-based sensors.

2. Experimental Methods

2.1. Materials

All chemicals, namely silver nitrate, sodium citrate, sodium borohydride, 4-mercaptobenzoic acid (4-MBA), HAuCl₄, H_2O_2, HCl, Ni

$(NO_3)_2 \cdot 6H_2O$, $NaNO_3$, KNO_3, $CaCl_2 \cdot 2H_2O$, $FeCl_2$, $FeCl_3$, $Cd(NO_3)_2 \cdot 4H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $HgCl_2$, and $Cu(NO_3)_2 \cdot 2.5H_2O$, were of ACS grade and were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Dimethyl sulfoxide (DMSO), sodium phosphate dibasic, sodium phosphate monobasic, and sodium phosphate were of ACS grade and were purchased from Acros Organic (Taichung City, Taiwan, ROC). Sodium phosphate dibasic (1.0 M) and sodium phosphate monobasic (1.0 M) were used to prepare phosphate buffer solution (PBS; 1.0 M; pH 7.4). Ultrapure water from a Milli-Q ultrapure system (Millipore, MA, USA) was used for all the experiments. Screen-printed carbon electrodes (SPCEs) were obtained from Zensor R&D (Taichung City, Taiwan, ROC).

2.2. Preparation of AgNP Seeds

The AgNP seeds were prepared through the sodium citrate- and sodium borohydride-mediated reduction of silver nitrate [28]. A 20-mL ultrapure water solution was heated to boiling, and three solutions, silver nitrate (100 mM, 50 μL), sodium citrate (100 mM, 50 μL), and sodium borohydride (5 mM, 1.2 mL), were subsequently added in sequence with vigorous stirring. The initially colorless solution was heated under reflux for an additional 30 min until it assumed a yellow color, indicating the formation of AgNPs. The AgNP solution was cooled to room temperature and stored at 4 °C. For simplicity, the concentration of the prepared AgNP solution is defined as 1×.

2.3. Electrochemical Fabrication of AgMF-SPCE Substrate

According to our previous study, a SERS-active AgMF-SPCE substrate was prepared through cyclic voltammetry, which was performed with a CHI 6124e electrochemical workstation (CH Instruments, Austin, TX) [28–30]. The three-electrode system consisted of the SPCE as the working electrode (geometric area, 3.14×10^{-6} m²), a Ag/AgCl reference electrode, and a platinum wire auxiliary electrode. Prior to the deposition process, a bare SPCE was preoxidized by applying a potential of 0.5 V for 10 min in 1.0 M PBS at pH 7.4 with continuous stirring. Subsequently, the electrochemical synthesis of AgMFs on the SPCE substrate was performed by cycling the potential between −0.3 and 0.3 V in a 10 mM $AgNO_3$ aqueous solution containing 4 mM sodium citrate at a scan rate of 2.5 mVs^{-1} for 15 cycles. After the electrochemical process, the AgMF-SPCE substrate was removed from the solution and rinsed thoroughly with ultrapure water.

2.4. Characterization

A JEM 2010 transmission electron microscope (TEM) (JEOL, Tokyo, Japan) was used to measure the morphologies of the prepared AuNPs and AuNSs. Energy-dispersive X-ray spectroscopy (EDS) (Oxford Instruments, Oxfordshire, UK) was used to confirm their compositions. An Evolution 200 UV–vis spectrometer (ThermoFisher, NY, USA) was used to measure the optical properties of the prepared AgNP, Au NP, and AuNS solutions.

2.5. UV–Vis and SERS Procedure for Mercury-Ion Sensing

Most of the metal salts used in this study were nitrates. Stock solutions of the metal ions (0.1 M) were prepared in 0.1 M HNO_3 and diluted to a metal concentration range of 0–1.0 mM with ultrapure water. For the selectivity study, 100 μL aliquots of metal ion solution premixed with 100-μL AgNP seed solution (0.1×) were added to 1.07-mL ultrapure water containing 80-μL $HAuCl_4$ (0.1%), 100-μL HCl (10 mM), and 50-μL H_2O_2 (0.3%). The mixtures were equilibrated at 60 °C for 60 min, then purified through centrifugation (RCF 10,620 ×g) for 10 min, and redispersed as pellets in 1.0 mL ultrapure water. Finally, the absorbance spectra were recorded using a Synergy H1 Hybrid Multi-Mode Microplate Reader (Biotek Instruments, Winooski, VT, USA).