



Short communication

A plasmonic mercury sensor based on silver–gold alloy nanoparticles electrodeposited on indium tin oxide glass



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ABSTRACT

We construct silver–gold alloy nanoparticles (Ag–AuNPs) as the basis of a reagentless, sensitive and simple mercury sensor. Ag–AuNPs were electrodeposited directly on transparent indium tin oxide film coated glass. Hg(II) ions in aqueous solution could be reduced by Ag atoms existing in Ag–AuNPs; the deposition/amalgamation of Hg on the nanoparticles resulted in a blue shift of the localized surface plasmon resonance peak. Therefore, Hg²⁺ can be detected quantitatively by using a spectrophotometer. The sensor response is linear in the range from 0.05 to 500 ppb of Hg(II) concentration. No sample separation or preconcentration is required for detection of ultralow levels of mercury in water samples. The results shown herein have potential applications in the development of a new optical sensor for the detection of low concentrations of mercury.

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1. Introduction

It is well known that mercury has been classified as a “priority hazardous substance” because of its toxicity, mobility, and long residence time in the environment [1]. It can pose serious adverse effects in the brain, kidney, nervous system and endocrine system in humans and animals [2]. The U.S. Environmental Protection Agency suggests that the acceptable limit is 2 ppb and the standards for drinking water quality in China set a limit value of 1 ppb for mercury [3]. Therefore, it is important to develop a method for the excellently sensitive, selective, and efficient detection of mercury in environmental analysis, food testing and biomedical assay.

Noble metal nanoparticles, particularly gold and silver nanoparticles, have generated great interest because of their strong localized surface plasmon resonances (LSPRs). The LSPR peak of metal nanoparticles is different from that of bulk materials and is sensitive to the nanoparticles' size, shape, and composition, degree of aggregation of the nanoparticles, and local dielectric environment of the surrounding medium. These unique optical properties of noble metal nanoparticles open up novel applications in biological and chemical sensors for the detection of Hg(II). So far, two main types of sensors have been developed according to the LSPR sensing mechanism: (a) metal nanoparticle aggregation, using a color change due to the aggregation based on a functionalized metal nanoparticle system with oligonucleotides, oligopeptides, and chemical functional molecules [4–6] and (b) local refractive index

changes, relying on the LSPR peak shift due to the variation in the local refractive index induced by molecular interactions at the surface of metal nanoparticles [7] or adsorption of mercury on the surface of metal nanoparticles [8–15].

Among them, the optical sensing of Hg(II) based on the optical properties Hg–M interaction has attracted great attention because it is simple, cost effective, and does not require organic or biological ligands. The Hg(II) ions can be reduced to Hg(0) in the sodium borohydride solution [8–12]. The mercury would be adsorbed onto the surface of metal nanoparticles and result in a blue shift of the LSPR peak of the metal nanoparticles. Moreover, the optical sensing of Hg(II) is also achieved by taking advantage of the redox reaction between Hg(II) ions and Ag nanoparticles [13–15]. Thus, this method requires no additional reagents. It is very favorable in field analysis. However, the instability of silver nanoparticles and low sensitivity limit its application in the detection of Hg(II).

Our approach takes advantage of the electronic and chemical properties of Ag–Au alloy or core/shell nanostructures. A charge compensation mechanism leads to an increased electron density within Ag, which yields a negative oxidation state to enhance the chemical stability [16,17]. Electrodeposition of metal nanoparticles on indium tin oxide (ITO) surface is facile and effective [18]. Herein, we report on the fabrication of an optical Hg(II) probe based on the electrodeposition of Ag–Au alloy nanoparticles (Ag–AuNPs) onto the surface of transparent ITO substrate. We demonstrate that an Ag–AuNP plasmonic probe retains the outstanding selectivity of the original sensor and presents a much higher sensitivity than that of the AgNP-based sensor. The high sensitivity shows excellent potential for monitoring traces of mercury in water sample without sample separation and/or sample pre-concentration.

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2. Experimental

2.1. Materials and apparatus

ITO glass (1.1 mm) was purchased from Suzhou NSG Electronics Co. Ltd. (Suzhou, China). All the reagents were of analytical quality and used as received. The water throughout the experiments was purified by a Milli-Q system. Electrochemical deposition and cyclic voltammograms were carried out with a RST 3100 electrochemical workstation (Zhengzhou Shiruisi Technology Co., Ltd., China). A conventional three-electrode system was used for all electrochemical experiments. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were performed using an S-4700 SEM (Hitachi, Japan). Transmission electron microscopy (TEM) image was obtained from Tecnai G20 (FEI, U.S.A.). The absorption spectra were measured with a Cary 60 spectrometer (Agilent, Australia).

2.2. Electrodeposition of Au–AgNPs onto ITO substrate

Au–AgNPs were prepared by direct electrodeposition. The ITO glass ($0.6 \times 4.0 \text{ cm}^2$) was cleaned by using dilute $\text{NH}_3 \cdot \text{H}_2\text{O}$, ethanol and water for 10 min sequentially in an ultrasonic bath. The electrolyte contained 0.14 mmol/L AgNO_3 , 0.06 mmol/L HAuCl_4 , 0.02 mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$, and 0.12 mol/L phosphate buffer solution (PBS, pH 8.0) and kept at 30 °C. Au–AgNPs were electrodeposited onto the ITO glass by applying cyclic voltammogram in the potential range of 0 to -0.9 V at 0.05 V/s for 30 cycles. Finally, the electrode was soaked in polyvinylpyrrolidone (PVP) solution (1 g/100 mL) kept at 30 °C for 0.5 h.

3. Results and discussion

3.1. Deposition and characterization of Au–AgNPs

The Au–AgNPs were deposited on the ITO glass substrate using the cyclic voltammetric method. Fig. 1A shows the UV–visible absorbance spectra of Au–AgNPs electrodeposited in various potential ranges. A well-shaped LSPR band was observed at all potentials. When the negative potential increased from -1.0 V to -0.7 V , the LSPR peak was red-shifted in wavelength. This was because the applied potential influences both of the nucleation and particle growth processes. The less negative potential applied in the deposition process would produce a lower density of metal nanoparticles on the ITO surface, which resulted in a large particle size. In this work, the potential range of 0 to -0.9 V was used in the next experiments.

Fig. 1B displays the UV–visible spectra for nanoparticles deposited with different Ag/Au ratios (the total molar concentration of noble metal was fixed to be 0.2 mmol/L). All Ag–AuNPs showed absorption bands located between the absorption bands of pure Ag and pure Au, and the absorption peaks shifted to red and showed a broader peak with decreasing Ag/Au ratios. For all of the investigation of Ag–AuNPs, there is only one absorption peak, which is an indication of Ag–Au alloy formation.

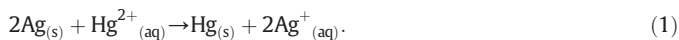
A typical SEM image of Ag–AuNPs electrodeposited onto the ITO substrate is shown in Fig. 1C. The nanoparticles are sparsely and randomly distributed on the surface of substrate with little aggregation. Size distribution of the Au–AgNPs (Fig. 1D) gives a diameter of approximately 53 nm. The EDS results show that the atomic percentage of Ag is about 82% (Fig. 1E), which is higher than 70% in electrolyte. This enhanced percentage may be attributed to the low deposition potential and electron value during the deposition of Ag.

Since these particles are deposited solidly on ITO, they cannot be released into water or ethanol upon sonication. Fig. 1F illustrates the

TEM image of Ag–AuNPs peeled off from the ITO substrate using a knife. It further demonstrated that the prepared nanoparticles were alloy. These results indicate that the electrochemical reduction could be regarded as a facile synthesis method to obtain particles immobilized on solid substrate without any organic stabilizers and linkers.

3.2. Sensing of mercury

Because the standard reduction potential of the Hg(II)/Hg couple (0.85 V) is higher than that of the Ag(I)/Ag couple (0.8 V), silver can be oxidized by Hg(II) ions according to the following redox reaction [14,19]:



The element mercury produced through this redox reaction was confined to the surface of the Ag–AuNPs. The deposition/amalgamation of mercury induced a blue shift of the LSPR peak wavelength of the Ag–AuNPs [20]. The changes in the LSPR band are the basis of the detection of the Hg(II) concentration. A disposable sensor can avoid the mechanical instability of repetitive deposition and stripping of mercury on metal nanoparticles indicated in a previous report [21].

The ratio of Ag/Au in electrolyte would determine the composition of Ag–AuNPs and their LSPR band. Fig. 2A shows the effect of Ag content in total metal electrolyte on the wavelength shift of absorption peaks for Ag–AuNPs in the presence of 0.5 ppm Hg^{2+} ions. The wavelength shifts of the LSPR peak reached maximum at the Ag content of 0.7 in electrolyte, corresponding to ~82% in the Ag–Au alloy. This magic number may be attributed to the special alloy structure. However, it is difficult to answer precisely because the relationship between peak shift and nanoparticles is very complex.

3.3. Analytical performances

We recorded the UV–visible absorption spectra of the Ag–AuNP film sensor and their corresponding colorimetric response after incubation different concentrations of Hg(II) (Fig. 3). With the increase of Hg(II) concentration, the color of the Ag–AuNP film sensor gradually turned from red to yellow and the intensity decreased after the reaction with Hg(II). Fig. 3B shows the linear plot of the LSPR peak blue-shift at variable Hg(II) concentration. The peak shift responded linearly to the Hg(II) concentration ranging from 0.05 to 500 ppb. The limit detection was estimated to be 0.02 ppb at a signal-to-noise ratio of 3, which is much superior to those of the assay based on AgNPs or AuNPs [11–15].

The selectivity of the assay for Hg^{2+} was investigated by testing the LSPR peak change of the film sensor to mercury and other metal ions, including Ag^+ , K^+ , Fe^{3+} , Co^{2+} , Pb^{2+} , Al^{3+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , and Ca^{2+} ions. The peak wavelength changes of the film sensor to various cations were illustrated in Fig. 3C. Under identical experimental conditions, only Hg^{2+} ions provoked a significant blue shift of peak wavelength to that of the original. As expected the other metal ions induced little changes for the Ag–AuNP film sensor, indicating that the method had a remarkable selectivity for Hg^{2+} ions.

The determination of Hg concentration in water samples was performed on the sensor. Tap water and lake water samples were collected from our laboratory and Dushu Lake (Suzhou, China). The Hg levels in tap and lake water were determined to be 0.61 ± 0.05 and 0.87 ± 0.06 ppb, close to the value of 0.67 and 0.83 ppb obtained by cold vapor atomic absorption spectrometry (CVAAS) according to the standard method in China. The recoveries for the assay of Hg^{2+} were 109 and 91% after addition of 1 ppb Hg(II).

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