



Shrink-induced ultrasensitive mercury sensor with graphene and gold nanoparticles self-assembly

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Abstract

Here we report an ultrasensitive trace mercury(II) micro sensor based on heat-shrinkable polymer (polyolefins, PO). The layer-by-layer self-assembly (LBL SA) method was employed to modify mixed gold nanoparticle (Au NPs) and graphene solution on a micro gold electrode with PO substrate. The unique wrinkle structure of the electrode surface and superior properties of modification film enhanced the performance of LBL SA graphene–Au NPs shrink sensor greatly in determination of Hg(II) using anodic stripping voltammetry (ASV): compared with a shrink gold electrode without surface modification, the sensitivity was improved for about 3.7 times from 0.197 to 0.721 $\mu\text{A/ppb}$; compared with a same-sized sensor without surface modification nor shrink, the sensitivity was improved for over 50 times. This sensor's detection limit of Hg(II) was achieved as 0.931 ppb with a sensitivity of 0.721 $\mu\text{A/ppb}$. This simple but highly sensitive sensor can be widely used in applications of on-line environmental monitoring of Hg(II).

1 Introduction

Heavy metal ions commonly distributes in natural environment, have posted significant threat to human health (Bader et al. 1999; Zhuang et al. 2009). Mercury(II) is the first place of highly toxic heavy metal ions, due to its bio-accumulation and bio-magnification abilities, mercury at a trace level in aquatic system is harmful to environment and human (Zahir et al. 2005; Sarajlić et al. 2013). For example, methylmercury, yields by microbial biomethylation of mercury(II), accumulates in bodies through the food chain, leading to the brain damage and other chronic diseases (Mergler et al. 2007; Harada 1995). Common methods employed for mercury(II) analysis were effective, general and sensitive, include atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), ion coupled plasma mass spectrometry (ICPMS), and microwave induced plasma atomic emission spectroscopy (MIP-AES) (Townsend et al. 1998; Gómez-Ariza et al. 2005; Harrington et al. 2004), but their process are too complex and

high cost, which limits their application for in situ measurements (And and Kounaves 1999). Therefore, further research should establish a highly sensitive and selective analytical method to determine ultralow concentrations of mercury for in situ environmental monitoring applications.

Current trend of in situ monitoring equipment is portable and miniaturization with micro sensor (Murdock et al. 2013). Anodic stripping voltammetry (ASV) can be implemented in portable equipment, is an extremely sensitive electroanalytical technique to detect trace mercury ions, contains pre-concentration step and stripping step with electrochemical measurements (Kokkinos et al. 2011; Shin and Hong 2010). An ASV sensor's performance is highly determined by its properties of electrode surface topography and material (Kokkinos et al. 2009). The micro sensor is limited by its small size, resulting in the low signal amplitude and sensitivity relatively (Davis and Higson 2013). Researchers in this field will thus need to develop novel innovations to solve the sensitivity and performance problem for miniaturized sensors.

Sensitivity of an ASV sensor is highly dependent on the surface area of working electrode that interfaces with the sample, rendering its problem of miniaturization (Zhang et al. 2015). Research in “high surface area” electrodes presents a smart solution to this problem in which one creates a rough micro- and/or nanostructured surface topography that considerably enhances the working

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electrode's electrochemically surface area (Hauke et al. 2017). While complex chemical deposition methods to this end have been available for many years (Dominik et al. 2016; Ghaemi et al. 2015), heat-shrinking a polymer substrate coated with metal thin film electrode could enhance electrochemically surface area more simply, the wrinkle structure greatly optimize the surface morphology (Wu et al. 2017). More over, fabrication of the shrink electrode is low-cost and does not require clean-room facilities or sophisticated equipment, this makes lower cost of sensors possible.

The layer-by-layer self-assembly (LBL) method based on electrostatic interactions represents a versatile and simple nanofabrication technique widely used to build three dimensional ultrathin multilayer films (Fang et al. 2010; Hillmyer et al. 2015). Recently, nanoparticle research has witnessed tremendous growth, metal nanoparticles have been widely applied to the fabrication of nanocomposites (Daniel and Astruc 2004). They have many excellent properties such as large surface-to-volume ratio, good electrical properties, strong adsorption ability, high surface reaction activity, small particle size and good surface properties (Abollino et al. 2010; Niu et al. 2016). These excellent properties are helpful for the immobilization of biomolecules. Graphene is a two-dimensional nanomaterial with a monolayer of carbon atoms packed in a honeycomb lattice. It has become one of the most studied material due to its remarkable properties, such as large surface area, excellent electrochemical stability, high conductivity and good mechanical stiffness (Li et al. 2008). Graphene has been applied in many critical areas, including energy conversion, sensors, solar cells, storage devices and reportedly made significant enhancements to the performance of electrochemical sensing.

Herein, we present a shrink polymer-based sensor that through layer-by-layer self-assembly method and heating-shrink process to construct the uniform and stereoscopic graphene and gold nanoparticles on the surface of shrink polymer. Heat-shrink process made shrink-polymer surface full of wrinkles. The wrinkles greatly increased surface area, uniform Au NPs were homogenously distributed onto the graphene nanosheet matrix, constructing a monodispersed Au NPs-based ensemble, this structure effectively improves the active reaction area. Meanwhile, the Au NPs could provide extraordinarily catalytic activity and good conductivity (Wang et al. 2011). This should greatly facilitate the sensitive measurement of Hg(II). The performance of this novel platform for stripping determination of Hg(II) is investigated in detail.

Encouragingly, such a shrink polymer sensor offers a remarkably improved sensitivity and detection limit. This sensor's detection limit (LOD) of Hg(II) was achieved as 0.931 ppb with a sensitivity of 0.721 $\mu\text{A/ppb}$, improved for

over 50 times. This simple but effective high-performance sensor construction method can be widely used in the development of highly sensitive ion sensor.

2 Experimental

2.1 Chemicals and reagents

Graphene suspension solution (PureSheetsMONO, 0.25 mg/ml) was received from Nanointegris Inc. Gold nanoparticles (3 mg/ml) dispersion solution was purchased from Nanjing Xiaomai Biotech Co., Ltd., China. Supporting electrolyte used was 0.5 M HCl buffer. Unless otherwise stated, deionized water (18.2 M Ω cm) used throughout all experiments was prepared from a Milli-Q system (Millipore, Milford, MA, USA). All the pieces of glassware were thoroughly cleaned with aqua regia and then washed repeatedly with Millipore water and acetone before using. All the chemicals were purchased from Sigma-Aldrich unless mentioned specifically.

2.2 Apparatus

Shrink film (polyolefins, PO) was purchased from Sealed Air. An Ag/AgCl (3 M KCl) (Tianjin Aidahengsheng Technology Co., Ltd., China) was used as calibration reference electrode. A Gold electrode was used as counter electrode. Measurement were performed with CHI660e electrochemical (Chenhua Instruments Corporation, China) controlled by a personal computer.

2.3 Self-assembly solutions preparation

The gold nanoparticles dispersion was diluted by water with volume ratio of 1:1, and then the equivalent volume graphene solution was dropped to gold nanoparticles solution, stirring for 5 min and left in the refrigerator (4 °C) for 24 h, solution evenly without precipitation.

2.4 Device fabrication

Figure 1 illustrated the fabrication process and the schematic structure diagram of the sensor. First, a 40 nm gold film was patterned on a PO shrink film substrate by sputter process for the electrode. Next, the mixed graphene and gold nanoparticles dispersion solution (graphene–Au NPs) and PDDA solution were layer-by-layer self-assembled on a micro sensor: Graphene–Au NPs solution and PDDA solution was dropped coating on the sensor for 5 min and dried by nitrogen alternately and repeated this process for five times. Then, the sensor was heated to shrink at 145 °C.

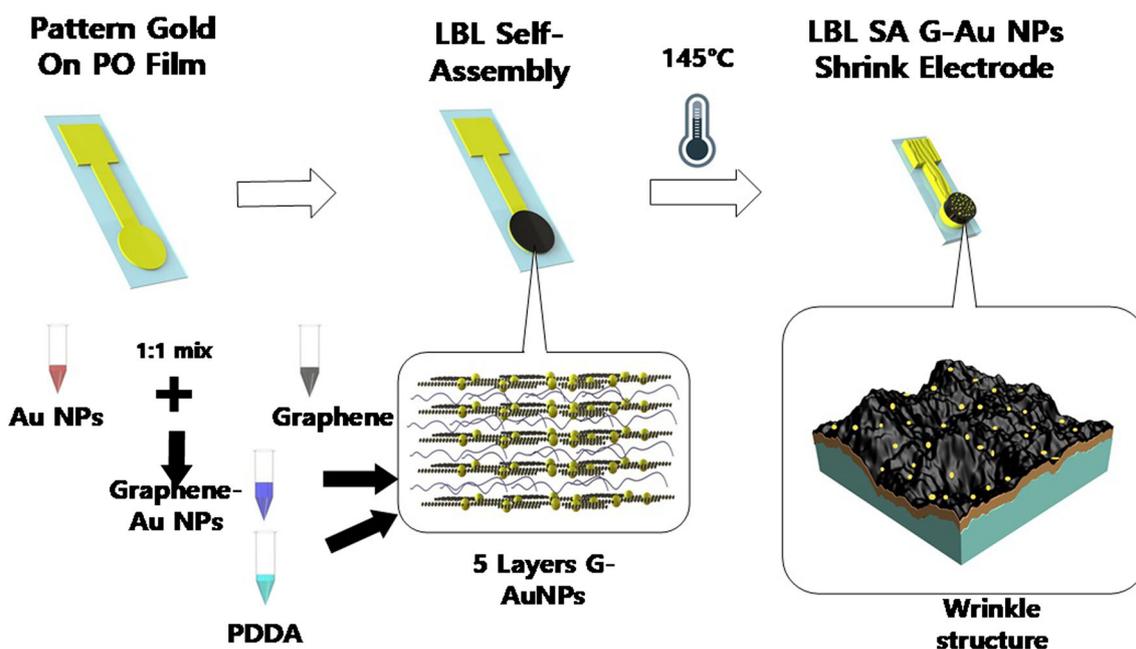


Fig. 1 Schematic diagram of an Hg(II) ultrasensitive sensor’s fabrication process and structure diagram of the sensor

2.5 Measurement procedure

The optimized voltammetry conditions to determine Hg(II) in acetate buffer were as follows: deposition potential (E_{dep}) = - 0.2 V whilst stirring or vibrating for 100 s, with 60 s quiescence time and a voltammetric scan from 0 to 0.8 V. The scan mode used the square wave modulation, frequency 25 Hz, step height 4 mV, pulse height 20 mV.

3 Results and discussion

3.1 Characterization

The optical image of the micro sensor on a PO polymer substrate was shown in Fig. 2a. As shown in Fig. 2b, the heat shrink process significantly changed the size of the device and created a surface full of wrinkles, effectively increasing the surface area in the unit size, so we could manufacture micro sensors with large surface area.

Due to the pre-stress effect, high temperature heating could shrink the PO plastic substrate:the surface area of the film significantly reduced, at the same time the thickness increased. To ensure the outcome, measurement of shrink ratio of a PO substrate was carried out. The PO substrate with radius of 3 mm were prepared for this experiment and heated in an oven for 5 min with different temperature. As shown in Fig. 3, when the temperature above 80 °C, PO plastic substrate starts to shrink evenly, the higher shrink

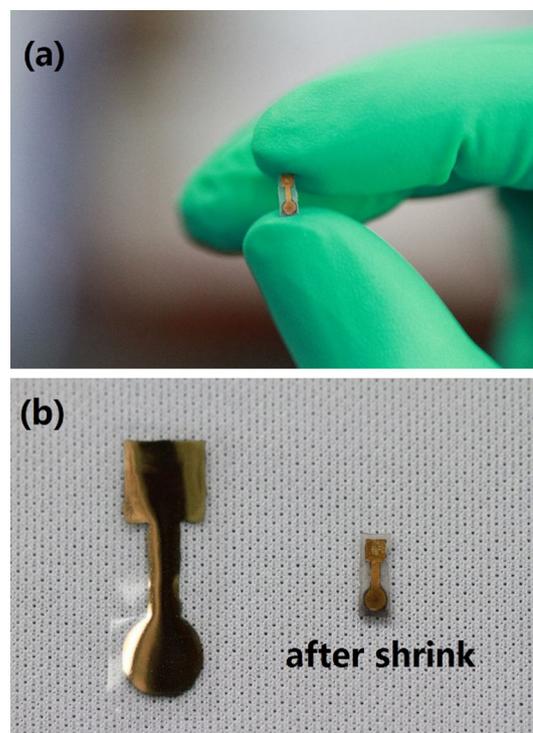


Fig. 2 a An optical image of the LBL self-assembly graphene and Au NPs sensitive sensor fabricated on a shrink polymer substrate. b Heating process significantly shrunk the size of the device and created a surface full of wrinkles

temperature results in a higher contraction ratio. When the temperature reaches 140 °C, shrinkage of PO substrate reaches its maximum, the temperature rise could not shrink

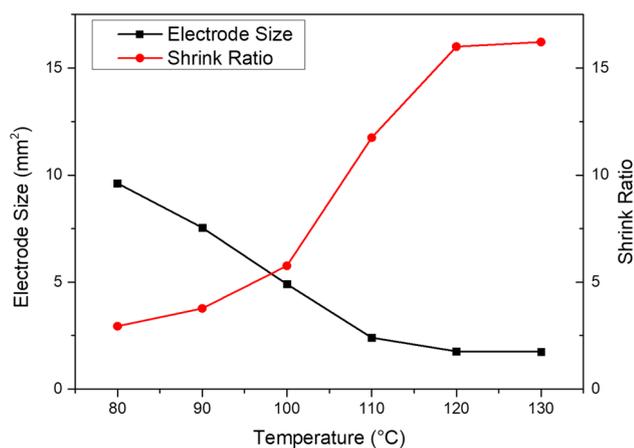


Fig. 3 The electrode size and shrink ratio of PO polymer substrate sensor with different temperature

the PO substrate further. Herein, the following equation was used for the shrink ratio calculation.

$$\text{Shrink ratio} = \frac{S_0}{S_T} \times 100\% \quad (1)$$

where S_0 is the initial area of the PO substrate and S_T is the area after heating at T °C. Sputtering and patterning the gold electrode on the PO substrate, when heated, because of the stress mismatch between the gold film and the PO substrate, the gold film appeared fold and presented wrinkle structure. From the equation for shrink ratio, the rate of surface area of gold film, relative to the substrate, is quantitatively calculated by the reciprocal of shrink ratio. As the heating temperature and the shrinkage ratio increase, wrinkle structure became more pronounced. Figure 4 shows the SEM images of the gold films on PO substrate and heating at 90 and 140 °C, respectively. From Fig. 3, the maximum shrinkage ratio is about 16, it means that there are 16 units area gold film folds on per unit area of the substrate. Huge increase of surface area could enhance the sensitivity of the electrochemical sensor significantly. We also photographed the LBL SA AuNPS graphene modification film. As shown in Fig. 5, Au nanoparticles with 20 nm diameter were uniformly distributed on the graphene nanosheet's surface, uniformly dispersed gold nanoparticles could effectively provide both active site and electrocatalytic activity, so the sensor with this modification film could reach lower detection limit (Xu et al. 2008).

3.2 Effect of LBL SA graphene–Au NPs film and shrink process for detection of Hg(II)

To characterize the effect of LBL SA graphene–Au NPs film and shrink process for detection of trace Hg(II) ion, a bare gold sensor (without any modification and without

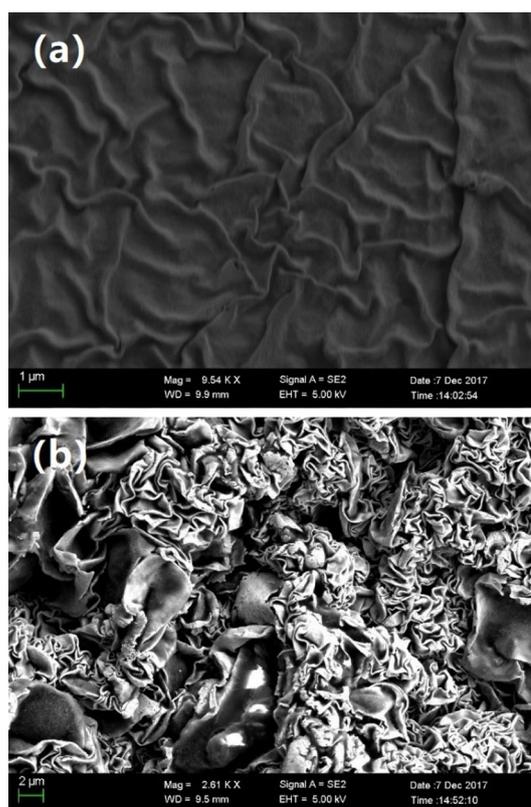


Fig. 4 a SEM image of gold film on a PO substrate heated at 90 °C; b SEM image of gold film on a PO substrate heated at 140 °C

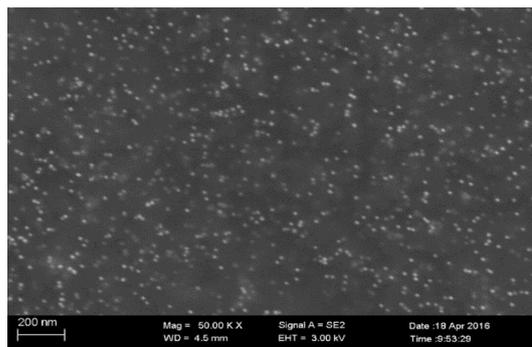


Fig. 5 SEM image of LBL self-assembled graphene and Au NPs film with 20 nm diameter gold nanoparticles uniformly distributed on the graphene nanosheet's surface

shrink), a LBL sensor (modification on bare gold sensor but without shrink), a shrink sensor (without any modification), a shrink first sensor (shrink first and then modification) and a LBL first sensor (modification first and then shrink) were tested in a series of solution with Hg(II) from 2 to 10 ppb, respectively. All the sensors were same-size. As shown in Fig. 6, both shrink process and LBL SA graphene–Au NPs film could enhance the sensitivity of the sensor at varying degrees. The LBL first sensor has the greatest sensitivity within the experimental group, compared with a shrink

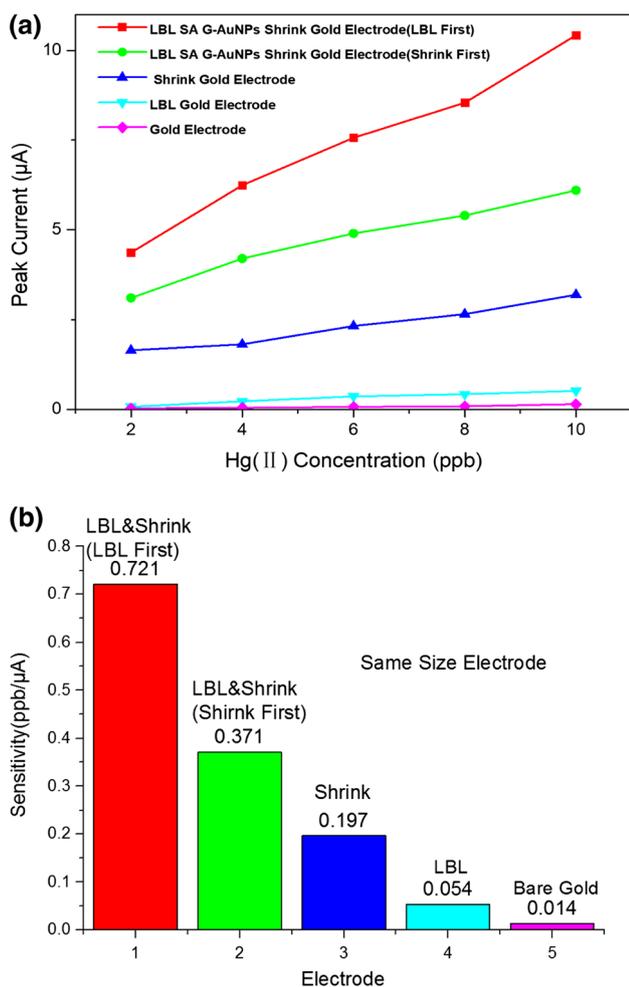


Fig. 6 Anodic stripping voltammetry results measured by the LBL SA graphene–Au NPs shrink sensor, non-modification, non-shrink, non-shrink and non-modification sensor and of Hg(II) from 2 to 10 ppb with 0.5 M HCl buffer solution. Sensitivity of LBL SA graphene–Au NPs shrink sensor increased about 3.7 times and over 50 times, respectively

gold electrode without surface modification, the sensitivity is improved for about 3.7 times from 0.197 to 0.721 µA/ppb; compared with a sensor without surface modification nor shrink, the sensitivity is improved for over 50 times. Compared the sensitivity of the Shrink sensor and the Bare Gold sensor, the ratio was slightly smaller than the PO substrate maximum shrink ratio that mentioned above, a possible reason is that some region of gold film was folded closure so that not fully contact the test solution (Zhang et al. 2013). Compared the sensitivity of the LBL first sensor and the shrink first sensor, we could find that the order of modification and shrink process affected the sensitivity of the sensor, a possible reason is that air was trapped in the wrinkle structure, causing our droplet assembly solution not fully contact the electrode surface, so the modification film cover the surface of the shrink first

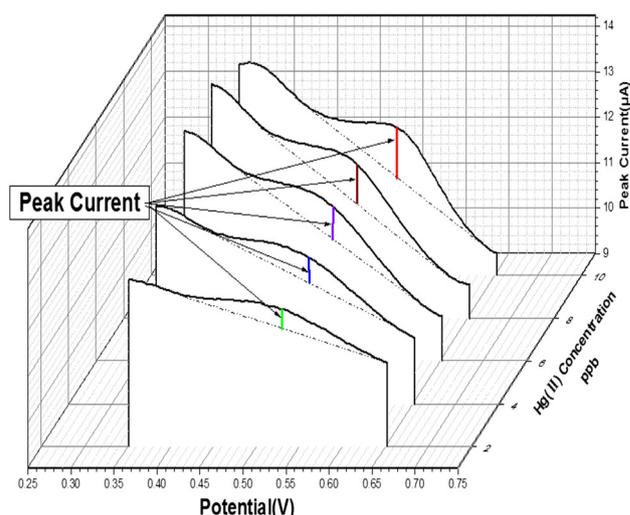


Fig. 7 Anodic stripping voltammograms of Hg(II) measured by the ultrasensitive sensor

sensor partially. Meanwhile, the LBL SA graphene–Au NPs shrink sensor’s output signal has also been significantly improved.

Properties of the electrode material and surface area highly determined the performance of an ASV sensor. In the process of mercury ion detection by ASV method, the mercury ion reduction reaction takes place in the pre-concentration stage, the reaction in the stripping stage is oxidation of mercury. In unit size, the wrinkles produced by the heat-shrink process greatly increase the surface area of the device, LBL SA graphene–Au NPs nanostructures also provided a large surface area, enriched more mercury ions in the pre-concentration stage. Gold nanoparticles can form an alloy with mercury, promote the enrichment of mercury ions, and on the one hand elevate the oxidation of mercury. Thus, we could observe that the stripping peak current increased significantly. Attributed to the stripping peak current increased, the sensitivity of the sensor improved significantly. It indicated that the self-assembled modified films shrink sensor shown significantly performance in mercury ions detection.

3.3 ASV determination of Hg(II)

The LBL self-assembly films modified shrink sensor’s performance was characterized with 0.5 M HCl buffer solutions containing a series of concentrations of Hg(II). We chose square wave anodic stripping voltammetry (SWASV) because this method can greatly reduce the background noise coming from the charging current during the stripping stage. Multiple SWASV scanning was used to remove the deposited mercury until the anodic stripping response disappeared. Meanwhile, the regeneration of the sensor surface was achieved. Deposition time was chosen

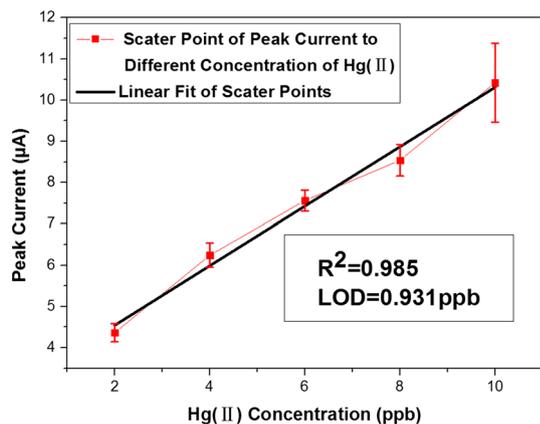


Fig. 8 Linear fitted calibration curve of Hg(II) from 2 to 10 ppb, with the limit of detection (LOD) derived as 0.931 ppb

to be 100 s to balance limit of detection and measurement time.

Stripping voltammograms were obtained from 2 to 10 ppb solutions with Hg(II) concentration increasing in 2 ppb steps, as shown in Fig. 7. Corresponding calibration is shown in Fig. 8, with five repeated measurements at each concentration. The detection limit is generally defined as three times the standard deviation of the noise. Sensitivity and limit of detection could be derived as 0.721 $\mu\text{A/ppb}$ and 0.931 ppb ($S/N = 3$) due to the high performance of LBL SA graphene–Au NPs modification and heating-shrink process, respectively, according to the corresponding linear calibration plot, linearity coefficient of determination of 0.985 was achieved for the fitted plot.

4 Conclusions

In summary, we presented a highly sensitive shrink polymer sensor for the determination of trace mercury. This sensor was based on a graphene–Au NPs hybrid nanocomposite. Such a nanostructured composite film constructed on surface full of wrinkle greatly enhanced surface area, facilitated electron-transfer processes and provided good electro-catalytic capacity, which improved sensing behavior for Hg(II) detection, leading to a remarkably improved sensitivity and detection limit (0.361 ppb). The sensor has the condition of application to portable mercury ion detection system. This simple but effective high-performance sensor construction method can be widely used in the development of highly sensitive ion sensor.

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