ULTRASENSITIVE MICRO SENSOR BASED ON LAYER-BY-LAYER SELF-ASSEMBLED GRAPHENE AND BISMUTH NANOPARTICLES FOR TRACE LEAD IONS DETERMINATION

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ABSTRACT

An ultrasensitive micro sensor for the detection of trace lead (II) is fabricated by mixed dispersion solution of bismuth nanoparticles (Bi NPs) and PDDA, and layer-by-layer self-assembled (LBL SA) with graphene (G) suspension solution on a micro gold electrode. The LBL SA G-Bi NPs sensor performance has been greatly enhanced in determination of Pb (II) using anodic stripping voltammetry (ASV). Compared with a sensor without surface modification, the sensor's stripping peak potential decreased from -0.520 V to -0.564 V, and its peak current increased from 1.227 μA to 8.372 μA. Compared with a sensor modified by LBL SA G (without Bi NPs), stripping peak potential decreased from -0.548 V to -0.572 V, the sensor's peak current increased from 0.284 μA to 1.263 μA. This sensor`s limit of detection (LOD) of Pb (II) was achieved as 0.078 ppb with a sensitivity of 1.061 μA/ppb. This simple but effective graphene−metal nanocomposites construction method can be widely used in the development of highly sensitive ion sensor.

INTRODUCTION

Heavy metal ions, especially lead (Pb) ion, commonly distributed in natural environment, have posted significant threat to human health [1]. Low concentration of lead has been proved to injure the peripheral/ central nervous system, and cause permanent impairment of cognitive development in children, including learning disability and decreased IQ [2]. Although atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), ion coupled plasma mass spectrometry (ICPMS), and microwave induced plasma atomic emission spectroscopy (MIP-AES) could be used to monitor Pb (II) [3], they are very expensive and not suitable for in-situ measurement. Therefore, further research should be undertaken to determine ultralow concentrations of lead for in-situ environmental monitoring applications.

Anodic stripping voltammetry (ASV) containing a pre-concentration step with electrochemical measurement, is an extremely sensitive electroanalytical technique to detect trace lead ions [4]. Due to good reproducibility, mercury film electrodes have been widely used in anodic stripping voltammetry. However, mercury is highly toxic and volatile, and long-term usage will be harmful to the health, causing serious environment pollution [5]. Bismuth is one of the most used materials to replace mercury-based electrodes due to its environmental friendly characteristics, and its ability to form "fused alloys" with heavy metals [6]. Bismuth film, a layer of stable solid film, performs much better stability than liquid mercury film. Bismuth film electrode background current is almost not affected by dissolved oxygen [7]. Bismuth-film electrode and polymer-modified bismuth film electrode are widely used not only for the determination of heavy metal ions, but also for the determination of organic compounds such as nitro phenols, drugs, pesticides and some bioactive substances. Research on bismuth film electrodes caught more and more attention [8].

Nano sensors have become one of the most active areas in environmental analysis [9]. Owing to unique capabilities, such as high surface area, increased mass transport, low detection limit, and better signal-to-noise ratio. Metal nanoparticles, especially Bi nanoparticles (BiNPs) assembled on various supports as modified electrodes have emerged as a promising alternative for the electro-analysis of Pb (II) [10]. Graphene, a single layer of sp^2 hybridized carbon atoms packed into a dense honeycomb two-dimensional lattice, has attracted tremendous attention from both experimental and theoretical scientific communities since experimentally produced in 2004 [11]. Due to its novel properties, such as exceptional thermal and mechanical properties, high electrical conductivity, graphene provides potential applications to synthesizing composites, nanoelectronics, electromechanical resonators, and ultrasensitive sensors. How to construct these functional materials is a worthy of study. Self-assembly is an important and effective strategy for nanofabrication that involves self-organizing the building blocks into functional structures by different driving forces [12].

Herein, we present a layer-by-layer self-assembly method to construct the uniform and stereoscopic graphene and bismuth nanoparticles on the surface of micro sensors. Uniform BiNPs were homogenously distributed onto the graphene nanosheet matrix, constructing a monodispersed BiNPs-based ensemble. It is worthy of noting that the as-prepared composite matrix in our work combines the advantages of the graphene nano sheets, with unique electrical conductivity and enlarged active surface area, together with BiNPs, which have extraordinarily catalytic activity and good conductivity. This should greatly facilitate the sensitive measurement of Pb (II). The performance of this novel platform for stripping determination of Pb (II) is investigated. Encouragingly, such a nanostructured composite film offers a remarkably improved sensitivity and detection limit.

This sensor`s limit of detection (LOD) of Pb (II) was achieved as 0.078 ppb with a sensitivity of 1.061 μA/ppb. This simple but effective graphene−metal nanocomposites construction method can be widely used in the development of highly sensitive ion sensor.

EXPERIMENTAL METHODS

Chemicals and Reagents

All the chemicals were purchased from Sigma-Aldrich unless mentioned specifically. Graphene suspension solution (Pure Sheets MONO, 0.25 mg/ml) was received from Nanointegris Inc. Bismuth nanoparticles (3 mg/ml) dispersion solution was purchased from Nanjing Xiaomai Biotech Co., Ltd., China. Supporting electrolyte used was 0.1 M NaAc/HAc buffer (pH 4.5). Unless otherwise stated, deionized water (18.2 MΩ·cm) is used throughout all experiments 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 in the experients.

Apparatus

Four-inch glass wafers 500 μm thick were purchased from Shanghai Gous Optics Co., Ltd., China. 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.

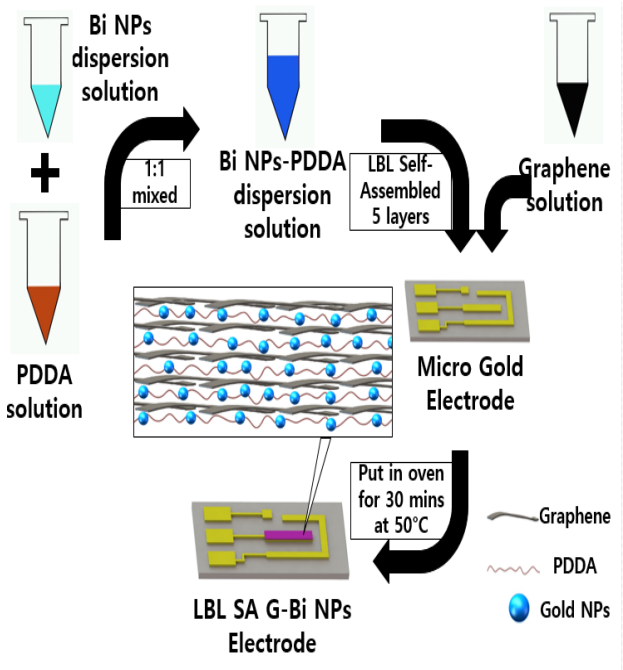

Figure 1: Schematic diagram of a Pb (II) ultrasensitive sensor's fabrication process and structure diagram of the sensor.

Self-assembly solutions preparation

The bismuth nanoparticles dispersion was diluted by alcohol with volume ratio of 1:3, and then the equivalent volume PDDA solution was dropped to bismuth nanoparticles solution, stirring for 5 minutes and left in the refrigerator (4°C) for 24 hours, and the solution is uniform without precipitation. Graphene suspension solution was used as received.

Device Fabrication

Figure 1 illustrates the fabrication process and the schematic structure diagram of the sensor. First, a 10 nm/100 nm chromium/gold film was patterned on a glass substrate by lift off process for the three-electrode sensor. Next, the mixed PDDA and bismuth nanoparticles dispersion solution (PDDA-Bi NPs) and graphene suspension solution were layer-by-layer self-assembled on a micro sensor: PDDA-Bi NPs solution and graphene suspension solution was dropped coating on the sensor for 5 mins, dried by nitrogen alternately, and repeated this process for five times. Figure 2 is an optical image of the sensitive sensor fabricated on a glass substrate. A working electrode (WE), a counter electrode (CE) and a reference electrode (RE) were integrated on the micro sensor. For ASV measurements, the WE is the electrode where the objective ions are reduced, so the LBL SA G-BiNPs film is modified on the working electrode.

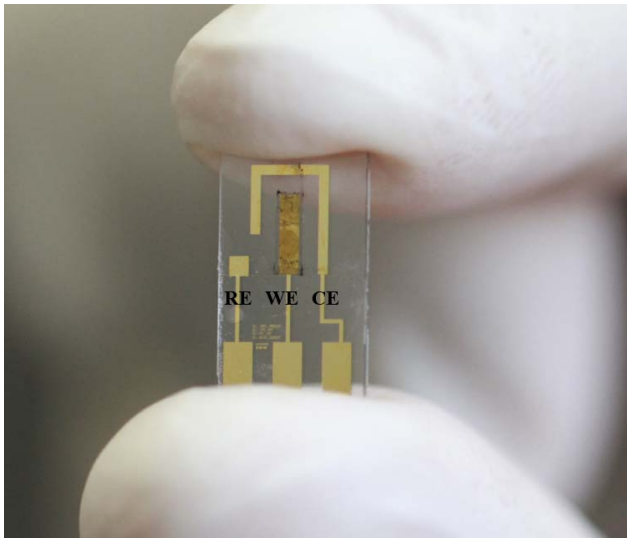

Figure 2: An optical image of the chemical sensor fabricated on a glass substrate.

Measurement Procedure

The optimized voltammetry conditions to determine Pb (II) in acetate buffer were as follows: deposition potential (E_{dep})= -1.2 V whilst stirring or vibrating for 240 s, with 60 s quiescence time, and a voltammetric scan from -1.2 to -0.4 V. The scan mode uses the square wave modulation, frequency of 25 Hz, step height of 4 mV, pulse height of 20 mV.

RESULTS AND DISCUSSION

Effect of LBL self-assembly films for detection of Pb

To characterize the effect of LBL self-assembly films for detection of trace Pb (II) ion, a bare gold sensor without any modification were tested in a solution with 100 ppb Pb (II). As shown in Figure 3(a), both sensors exhibites conspicuous current peaks. A weak stripping current peak (1.227 μA) of the bare gold electrode was observed, and the stripping peak current of LBL SA G-BiNPs electrode increased significantly (8.372 μA). In the meanwhile, the stripping peak potential of experiments decreased from -0.520 V to -0.564 V. To further explore the effect of bismuth nanoparticles for Pb (II) ion detection, another sensor modified by LBL SA Graphene without BiNPs was tested in 1 ppb Pb (II) solution. As shown in Figure 4(b), the peak current increased from 0.284 μA to 1.263 μA, and the stripping peak potential decreased from -0.548 V to -0.572 V.

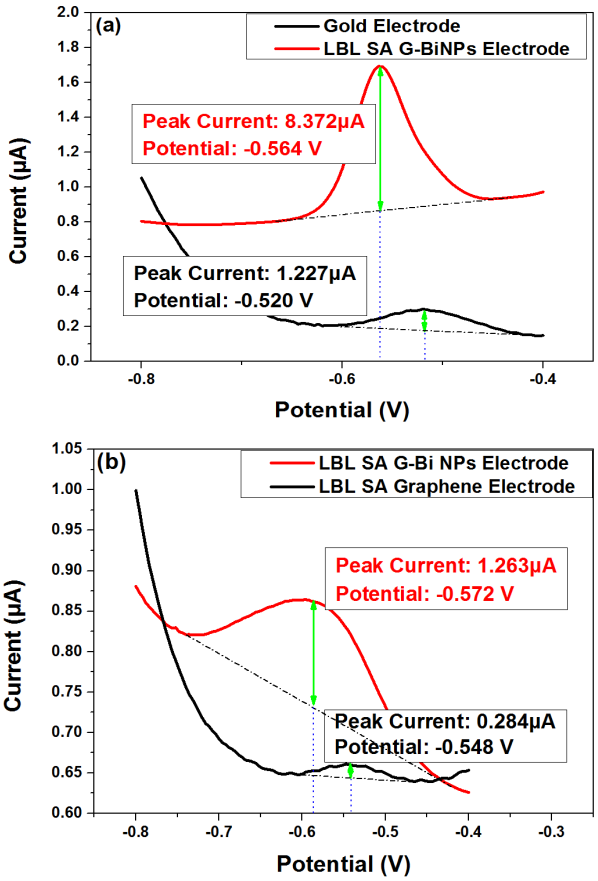

Figure 3: Anodic stripping voltammograms of (a) 100 ppb Pb (II) using a bare sensor and LBL SA G-Bi NPs sensor. (b) 1 ppb Pb (II) using a LBL SA G sensor and LBL SA G-Bi NPs sensor.

Performance of an ASV sensor is highly determined by properties of the electrode material and surface roughness [13]. In the process of lead ion detection by ASV method, the lead ion reduction reaction takes place in the pre-concentration stage, the reaction in the stripping stage is oxidation of lead. LBL SA G-BiNPs nanostuctures, with a large surface area, enriched more lead ions in the pre-concentration stage. Bismuth nanoparticles can form an alloy with lead, promoting the enrichment of lead ions. On the other hand, it can elevate the oxidation of lead, which was clearly observed from the stripping peak oxidation potential reduction. Attributed to the stripping peak current increased, the sensitivity of the sensor improved significantly. It indicates that the self-assembled modified films had better electro-catalysis towards Pb (II), and bismuth NPs showed significant performance.

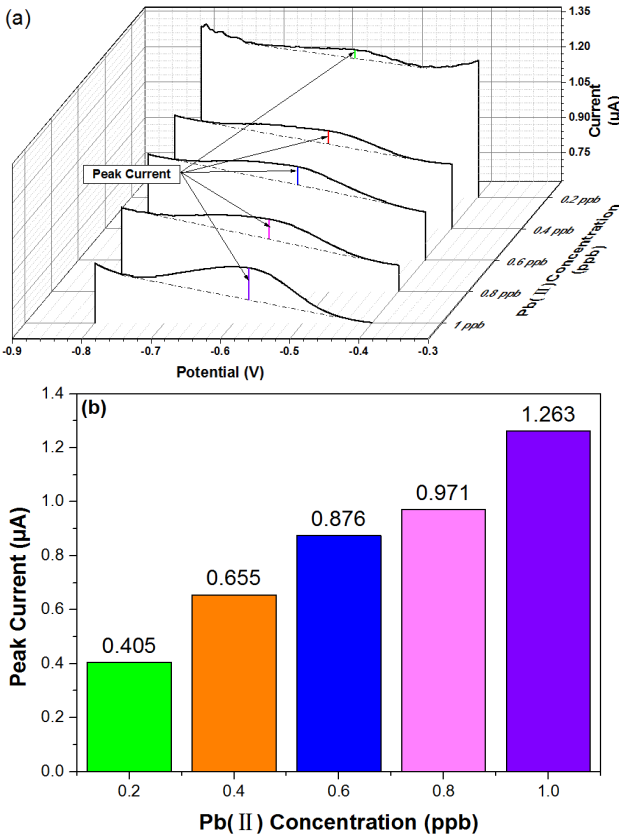

Figure 4: (a) Anodic stripping voltammograms (b) Histogram of peak current of Pb (II) measured by the ultrasensitive sensor.

ASV Determination of Pb (II)

Performance of sensors with LBL self-assembly films was characterized with 0.1 M NaAC/HAc buffer solutions (pH=4.5), containing a series of concentrations of Pb (II). Square wave anodic stripping voltammetry (SWASV) was chosen because this technique can greatly reduce the background noise from the charging current during the stripping stage. Multiple SWASV scanning was used to remove the deposited mercury until the anodic stripping response disappeared. The regeneration of the sensor surface was achieved. Deposition time was chosen to be 5 minutes to balance detection time and limit of detection.

Stripping voltammograms were obtained from 0.2 to 1 ppb solutions with the Pb (II) concentration increasing in 0.2 ppb steps, as shown in Figure 4(a). Figure 4(b) demonstrates that the peak current was increased with the concentration of Pb (II). Corresponding calibration is shown in Figure 5, with 5 repeated measurements at each concentration. Sensitivity and limit of detection could be derived as 1.061 μA/ppb and 0.078 ppb (S/N = 3) due to the high performance of LBL SA G-BiNPs modification, respectively, according to the corresponding linear calibration plot. Linearity coefficient of determination of 0.990 was achieved for the fitted plot.

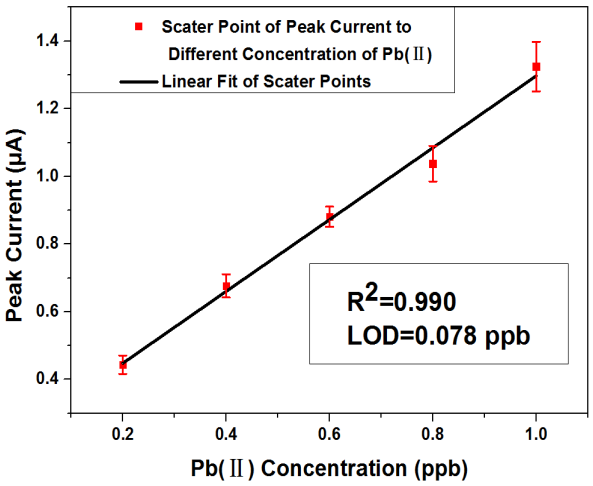

Figure 5: Linear fitted calibration curve of Pb (II) from 0.2 to 1.0 ppb, with the limit of detection (LOD) derived as 0.078 ppb.

CONCLUSION

In summary, we present a highly sensitive new thin film sensor for the determination of trace lead. This sensor is based on a Graphene-BiNPs hybrid nanocomposite. Such a nanostructured composite film greatly facilitates electron-transfer processes, enhances surface area and provides good electro-catalytic capacity, which improves sensing behavior for Pb (II) detection, leading to a remarkably improved sensitivity and detection limit (0.078 ppb). The sensor may result in applications to portable lead ion detection systems. This simple but effective graphene−metal nanocomposites may be widely used in the development of highly sensitive ion sensors.

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