MINIATURIZED FLEXIBLE SENSOR WITH REDUCED GRAPHENE OXIDE/CARBON NANO TUBE MODIFIED BISMUTH WORKING ELECTRODE FOR HEAVY METAL DETECTION

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ABSTRACT

A solvothermal-assisted Reduced Graphene Oxide (RGO) and Carbon-nano-tube (CNT) composites were successfully micro-patterned on a flexible Polyimide (PI) substrate using a lithography technique followed by the electrodeposition of Bismuth (Bi) on micro-patterned composite electrode surface for the electrochemical detection of heavy metal ions. The integrated electrochemical micro-sensor was then measured and evaluated for the detection of Cadmium and lead-heavy metal ions in an acetate buffered solution using Square Wave Anodic Stripping Voltammetry (SWASV) technique. The detection limit of 0.2 ppb and 0.6 ppb were recorded for the lead and Cadmium, respectively.

INTRODUCTION

Heavy-metal-ion sensors are significant tools for environmental and food-analysis research areas. The concern is the severe damages cause by these heavy metal ions [1]. Among them, Lead and Cadmium have received particular recognition due to the toxicity and environmental-pollution impacts [2]. However, due to low cost and easy operation, electrochemical sensors have been developed for the detection of heavy metal ions [3]. Moreover, square wave anodic stripping voltammetry (SWASV) is an electrochemical method that is generally used for heavy-metal-ion detection due to more effective selectivity and high sensitivity [4].

In most of the cases, mercury-film electrodes are preferred for their excellent stripping characteristics, however, the toxicity of mercury limits its wide applicability, especially in the cases that involve water contact. Recently, a bismuth-film electrode has been recognized as a promising substitute for the mercury electrode due to low toxicity, large cathodic-potential range, and an insensitivity to dissolved oxygen [5, 6]. However, the sensitivity and low detection limit of bismuth-based electrochemical sensors are inadequate compared to those of the conventional techniques such as atomic-absorption spectrophotometry, mass spectrometry and inductively-coupled-plasma mass spectrometry [7]. Therefore, the development of a heavy-metal-ion sensor with a high sensitivity is practically significant. Previously, a large amount of work has been performed regarding electrode-surface modifications to increase the sensitivity of metal-detection methods [8-11]. Among those research, the graphene modified working electrodes are alternative due to their electrochemical properties.

Graphene based nanomaterials have attracted intense interest regarding a wide range of applications due to their unique 2D structure and remarkable advantages that include a large surface area and chemical stabilities [12]. Recently, RGO has received increasing attention due to its applicability for the production of electronics and electrochemical systems [13, 14]. The solvothermal reduction of graphite oxide is one of the popular techniques due to simple setup, sound scalability, and an ability to recover the π-conjugation networks at the high temperature and pressure [15]. Nowadays, in order to improve the performances of synthesized materials, RGO based composites were developed for specific applications [16].

In this work, the synthesis of RGOCNT composites were synthesized through modified solvothermal method. Furthermore, the micro-fabrication process was used for the patterning working electrodes. After an in situ deposition of the bismuth film on the working Au/RGOCNT electrode, a fully integrated sensor with three electrodes was developed and characterized for tracing Cd and Pb ions using SWASV. The fabricated sensor is flexible, cheap, and reliable in real sample analysis. It also provides fast response and high sensitivity.

EXPERIMENTAL

Materials

Vtec PI 1388 polyimide liquid (RBI Inc., USA) was used as the flexible substrate. SU-8 2015 (Microchem, USA) was used as the mold for patterning active materials. The standard solutions of the metals (Cd ion, Pb ion, Bi ion), the graphite powder (44-μm size), the -D (+) glucose, the Ethanol, the sodium acetate, and the glacial acetic acid were purchased from Aldrich Co. (St. Louis, U.S.A.). Acetate-buffer solution (0.1 M) served as the supporting electrolyte for the detection of the heavy metals. Deionized water (resistivity • 18 M .cm) was used in every experiments. All he electrochemical measurements were carried out in a 20 mL cell.

Apparatus

We carried out the electrochemical characterization of the fabricated heavy metal ions sensor by using electrochemical analyzer (CHI 660E, CH instruments, USA) at room temperature. The physical characteristics of the active materials were investigated using field emission scanning electron microscopy (FESEM).

Fabrication

Figure 1 (a) shows the fabrication sequence of the proposed sensor. First, a PI substrate layer was deposited on top of the silicon substrate. After that, a Cr and Au film was sputtered on top of the PI layer, it was patterned with three different electrodes using the wet-etching technique. Next, the photolithography technique was used to cover the sample with an SU-8 photoresist, whereby the working electrode was excluded. Then, after active material suspension was spray-cast on it, the working electrode was dried in the air at room temperature.

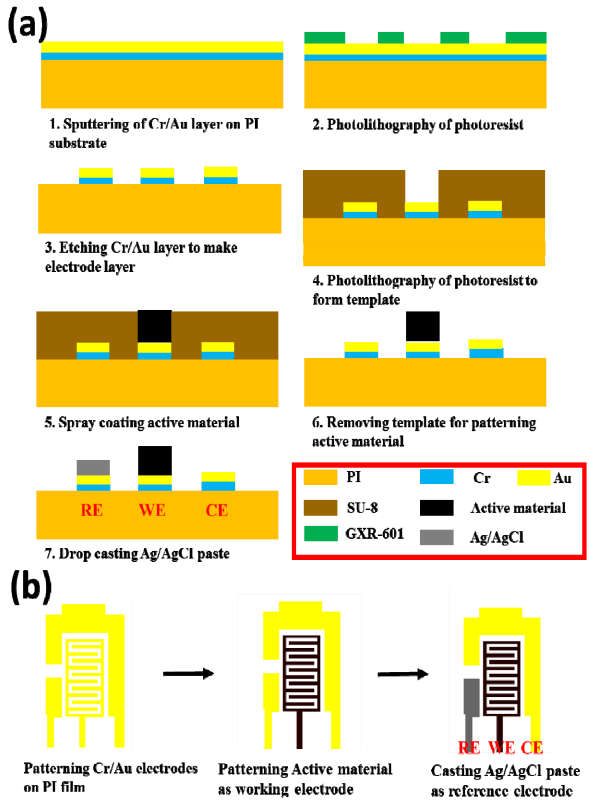

Figure 1: (a) Fabrication procedure of proposed flexible heavy metal ions sensor based on PI substrate. (b) Top view of whole fabrication process.

Next, the photoresist was removed from the sample using a PG-remover, and it was then washed away by IPA and deionized water. Lastly, Ag/AgCl paste was cast on top of the reference Au electrode. Figure 1 (b) shows a top view of whole process.

Measurement procedure

The heavy metal ions sensor was applied using an in situ electroplating Bi, whereby the fabricated device was immersed in 20 mL of the target ions standard solution. The SWASV analysis of the Cd and Pb ions were performed in 0.1 M acetate-buffer solutions in the presence of 400 ppb of Bi^{3+}. The SWASV mode contains a time-controlled electrochemical deposition and a positively applied potential square-wave stripping scan. The parameters are as follows: E_{dep} = 150 s; t_{eq} = 20 s; E_{begin} = -1.4 V, E_{end} = -0.6 V, E_{step} = 5 mV, E_{ampl} = 25mV, and f = 25 Hz. Prior to the next cycle, a 60 s clean step at 0.1 V was performed to remove the residual bismuth. A magnetic stirrer was used to stir the test solutions during the electrodeposition and cleaning steps.

RESULTS AND DISCUSSIONS

Figure 2 (a) and (b) show the surface morphology of the Au/RGOCNT electrode, whereby it is clearly observed that a rippled crumpling structure is on the RGO sheets. This crumpling structure is supposedly caused by the reduction of the oxide groups in the RGO sheet. Furthermore, CNTs are observed between RGO sheets to improve the surface area. This crumpling structure is supposedly caused by the reduction of the oxide groups in the RGO sheet.

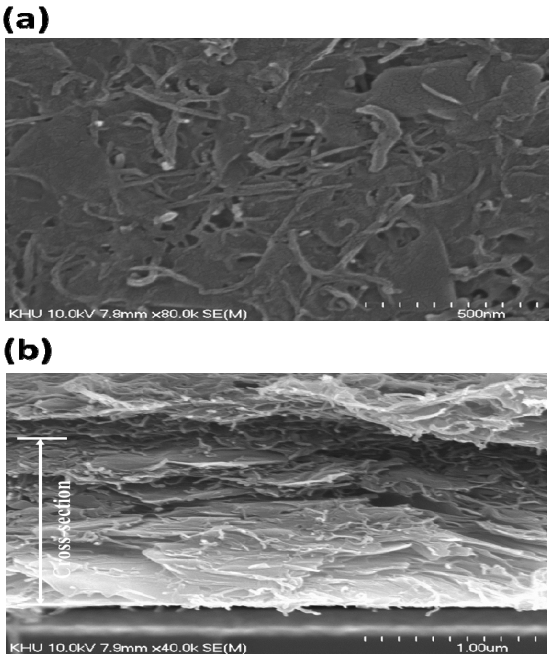

Figure 2: Scanning-electron images showing the morphology of the RGOCNT composite electrode. (a) Top view and (b) cross-section view.

Furthermore, CNTs are observed between RGO sheets to improve the surface area. These results indicates that RGOCNT composite was successfully synthesized. Figure 3 shows the fabricated sensor.

Cyclic voltammograms (scan rate = 50 mV/s) of the modified different electrodes and normal Au electrode in a 0.1 M KCl solution containing 2 mM $K_3[Fe(CN)_6]$ are shown in Figure 4. On the Au electrode, a pair of weak redox peaks was observed. While on the Au/RGO electrode, higher peak currents was observed during CV analysis. This results is caused by the unique nanostructure of the RGO sheet. The Au/RGOCNT10-1 electrode shows the highest peak currents during CV analysis. After adding CNTs, the modified electrode's surface area significantly increased.

Figure 5 shows the square wave anodic stripping voltammograms of 300 ppb Cd and Pb ions at Au/Bi, Au/RGO/Bi, Au/RGOCNT5-1/Bi, and Au/RGOCNT10-1/Bi. As shown in Figure 5, two weak peaks were observed on the Au/Bi electrode. In contrast, the Au/RGO/Bi exhibited higher stripping responses toward Cd and Pb ions detections. After modifying with RGOCNT composites, the striping peak was increased in comparison with Au.RGO/Bi electrode. The highest stripping peaks were observed on the Au/RGOCNT10-1/Bi electrode.

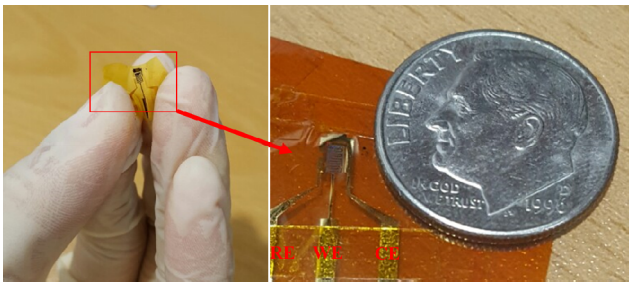

Figure 3: Photograph of fabricated flexible sensor.

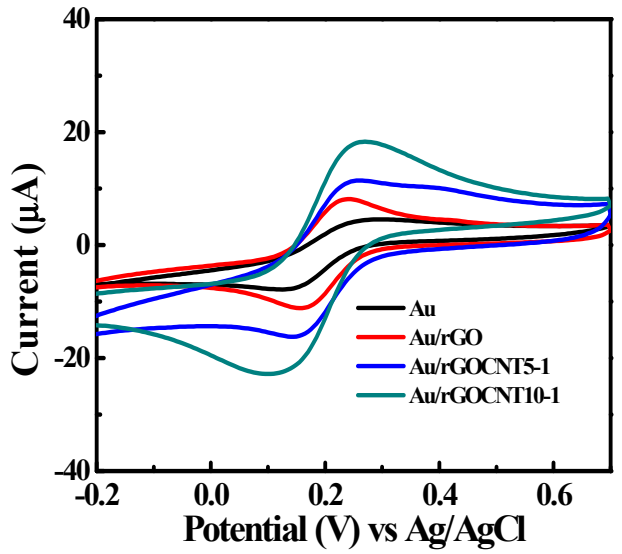

Figure 4: Cyclic voltammogram of different working electrodes. Au electrode (black line), Au/RGO electrode (red line), Au/RGOCNT5-1 electrode (blue line) and Au/RGOCNT10-1 electrode (green line).

The fabricated electrochemical sensor was calibrated in 0.1 M acetate buffer solution before the Cd and Pb heavy metal ions measurement. Under experimental measurement procedure, a series of SWASV voltammograms with increasing concentrations of Cd and Pb ions were recorded. Stripping voltammograms with well-defined, undistorted peaks are depicted in Figure 6. The fabricated sensor displayed linear responses towards Pb and Cd ions in the concentration range from 20 to 150 ppb. The stripping peak current and the concentrations of the Cd and Pb ions exhibited a favorable linear relationship.

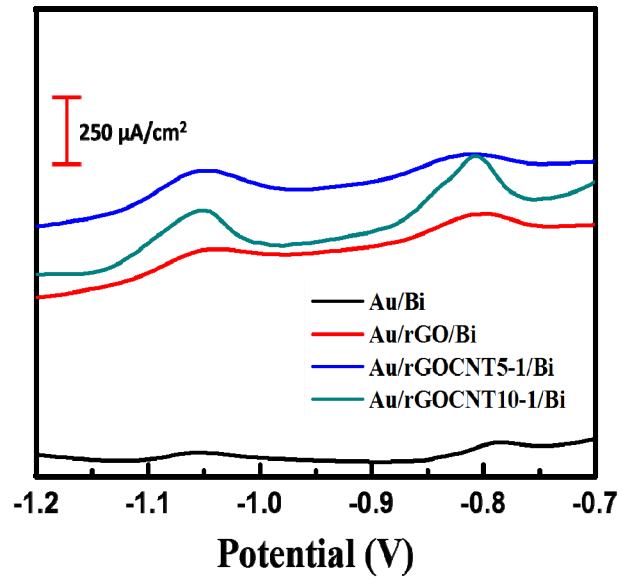

Figure 5: Stripping voltammograms of Au/Bi (black line), Au/RGO/Bi (red line), Au/RGOCNT5-1/Bi (blue line) and Au/RGOCNT10-1/Bi (green line) in acetate-buffer solution containing 300 ppb of Cd and Pb ions.

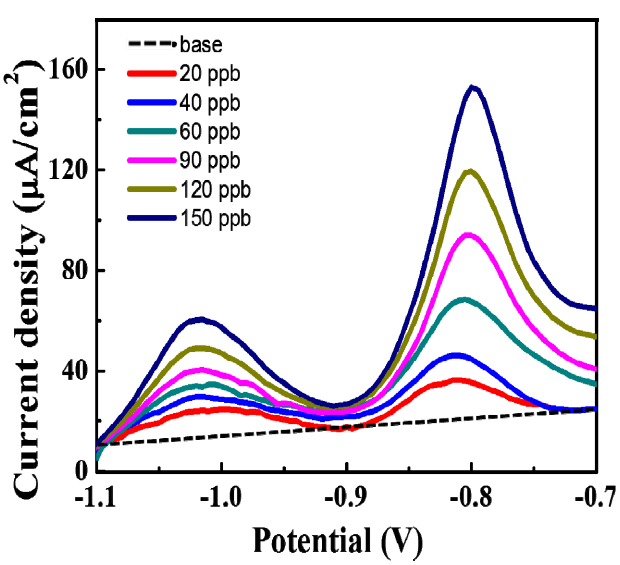

Figure 6: Square wave anodic stripping voltammograms for different concentrations of Cd and Pb ions at the in situ plated Au/RGOCNT10-1/Bi in 0.1 M acetate buffer solution (pH 4.5) containing 400 ppb Bi.

For the Cd ion, the sensitivity is 264 nA/ppbcm^2, with a correlation coefficient of 0.982. For the Pb ion, the sensitivity is 897 nA/ppbcm^2, with a correlation coefficient of 0.992.

To evaluate the applicability and feasibility of the developed sensor, the flexible MEMS sensor was applied to detect Cd and Pb ions in real water samples using optimized conditions. Figure 7 illustrates the typical stripping voltammograms of three standard additions. The fabricated sensor exhibits good linearity, indicating the availability of the proposed sensor in real sample analysis.

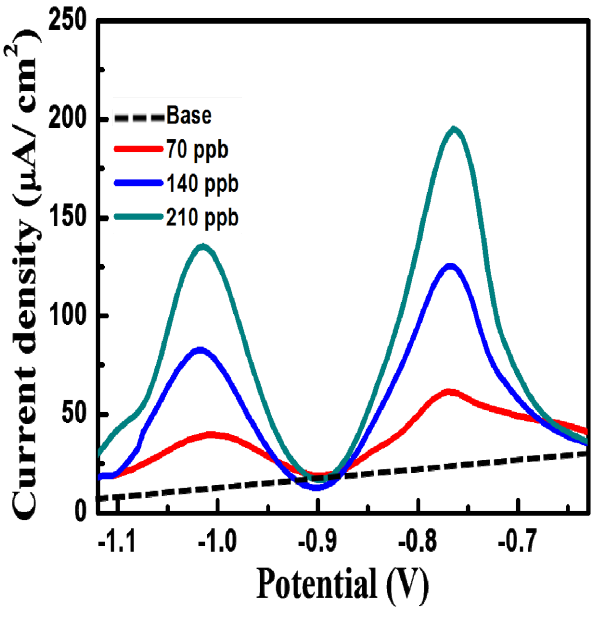

Figure 7: Typical stripping voltammograms for the determination of heavy metal ions in drinking water using standard addition method under optimized conditions. The concentration of both Cd and Pb ions for each addition is 70 ppb.

CONCLUSIONS

In this work, a flexible electrochemical heavy metal ions detection sensor based on Au/rGOCNT10-1/Bi working electrode was newly developed, and further used for simultaneous determination of Cd and Pb ions by SWASV. With the excellent properties of RGOCNT10-1 film and good stripping characters of Bi, the developed sensor exhibited sharp and high peaks for target heavy metal ions. The developed sensor exhibited many advantages over traditional heavy metal ions sensors, such as large surface area of working electrode, good sensitivity, and stability. In addition, the simple and green fabrication method greatly expands the scope towards the mass-production of "mercury-free" sensors for heavy metal analysis, which hold great promise for their wide application in environmental and food analysis.

ACKNOWLEDGEMENTS

This work was partially supported by the Technology Innovation Program (10065696) funded By the Ministry of Trade, industry & Energy (MI, Korea) and the ICT R&D program of MSIP/IITP [2015(R0101-15-0147), Implantable Biosensor and Automatic Physiological Function Monitor System for Chronic Disease Management]. The authors are grateful to MiNDaP (Micro/Nano Devices & Packaging Lab.) group members at the Department of Electronic Engineering, Kwangwoon University, for their valuable technical discussion and supports.

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