A SUB-PPB-LEVEL INTEGRATED ELECTROCHEMICAL HEAVY METAL ION MICROSENSOR

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ABSTRACT

This paper reports a miniaturized on-chip electrochemical sensor with integrated microchannel and bismuth (Bi) planner electrode for detecting trace amount of Pb^{2+} ions by anodic stripping voltammetry (ASV). A low limit of detection (LOD) of 0.3 ppb and is achieved. The result is promising for trace heavy metal ion detections in industrial and residential water quality monitoring and treatment applications.

INTRODUCTION

Toxic heavy metal ions (Pb^{2+} , Cd^{2+} , Co^{2+} , Cr^{2+} , etc.) possesses severe threats to public health, due to the increasingly serious pollution worldwide. A rapid and accurate detection technology is thus in great demand. Lab tests use high-end instruments like inductively coupled plasma mass spectrometer and ion chromatography are bulky, expensive, time-consuming and limited usage for in situ environmental screening and monitoring, while less-expensive test papers and ion-selective electrodes suffer from severe ion cross-sensitivity, low sensitivity, or short operation lifetime. Therefore, it is of critical importance to develop a high-performance, cost-effective heavy metal ion detection platform for portable applications. Among the effective methods, electrochemical measurement of anodic stripping voltammetric analysis is recognized as the most sensitive electroanalytical technique [1-5].

Anodic stripping voltammetry (ASV) is considered one of the most sensitive methods for trace-amount determination of many metals and compounds in environmental and biological samples.

Various materials have been used to form working electrodes of ASV sensors. Bismuth (Bi) is advantageous over mercury, Au [6], and carbon [7], due to the near-zero toxicity, wide potential window, and insensitivity to dissolved oxygen. It should be noted that several electrochemical heavy metal ion sensors have been reported using an assembled bulk electrochemical cell setup [8, 9]. In contrast, on-chip microsensors require using integrated circuit (IC) compatible materials and fabrications.

Here, we present a miniaturized ASV heavy metal ion sensor utilizing a Bi based thin-film working electrode (WE) formed via conventional evaporation and photolithography (Fig. 1a). Compared to Bi electrodes formed by *in situ* method, in which extra Bi^{3+} ions are added in the analyte solution and then co-electrodeposited with the target analyte metals to compensate for material consumptions [10] during ASV measurements (Fig. 1b), our *ex situ* Bi electrode will enable rapid test and mass production of sensors. Particularly, the microsensor consists of a Bi WE, a silver/silver chloride (Ag/AgCl) reference electrode (RE), and an Au counter electrode (CE) (Fig. 1c), embedded inside a microfluidic channel for the ASV detection of heavy metal ions in a miniaturized format (Fig. 1d).

EXPERIMENTAL

Following materials were used to prepare 0.1 M acetate buffer solution (pH = 4.6): 0.1 M Acetic acid (Fisher Scientific, Fair Lawn, NJ), 0.1 M sodium acetate (Sigma-Aldrich, St. Louis, MO), 0.1 M NaCl (Fisher Scientific, Fair Lawn, NJ), and deionized (DI) water. All electrochemical measurements were prepared from 1000 ppm Pb^{2+} (Sigma-Aldrich, St. Louis, MO) and Cd^{2+} (Fisher Scientific,

Figure 1: (a) Schematic of the electrochemical sensor and signal reading circuit. (b) Selective anodic stripping voltammetry (ASV) method. (c) Photos of the 3-electrodes prototype. (d) A sensing unit example with two sensors in the microchannel.

Fair Lawn, NJ) stock standard solution. Necessary dilutions were prepared with acetate buffer solution for various concentration study.

Standard fabrication processes were used to prepare the micro-sensor. A SiO₂ layer (300 nm thickness) was first grown on a silicon wafer via thermal oxidation. After a Ti/Au (5/80 nm thickness) layer was deposited on top of SiO₂ using e-beam evaporation, three Ti/Au electrodes were patterned via photolithography and wet chemical etching. Next, Ti/Bi (5/150 nm thickness) was deposited using e-beam evaporation and then patterned to form a WE on the surface of a Ti/Au electrode using a lift-off process. The same process was employed to form a Ti/Ag (5/500 nm thickness) electrode. Further, the device was immersed in a 0.1 M FeCl₃ solution containing 0.1 M HCl for 10 s to form a Ag/AgCl RE. Last, a poly(methyl methacrylate) or PMMA microfluidic channel (length: 8 mm; width: 1.5 mm; depth: 0.1 mm) was formed using hot embossing and then bonded with the substrate using an ultraviolet adhesive (PermiNex 2010, MicroChem, Westborough, MA). The sensing area of the WE is about 0.2 mm².

Square wave ASV was used to perform ion measurements. A deposition potential of -1.4 V was applied for 30 s, followed by applying a potential scan voltage from -1.4 to 0 V with an amplitude of 25 mV, a pulse width of 50 ms, a potential step of 4 mV, and a frequency of 5 Hz.

RESULTS AND DISCUSSION

Figure 2: Effect of (a) the deposition potential and (b) deposition time on the stripping peak current of 100 ppb of Pb²⁺ in acetate buffer (pH 4.6).

Fig. 2a shows the effect of deposition potential in a range from -1.8 V to -0.8 V on the stripping peak current of 100 ppb Pb²⁺ at a deposition time of 30 s. As the deposition potential positively increased to -1.4 V, the highest peak current was observed. After that, the peak current declined significantly due to the enhancement of electrolytic hydrogen evolution. Thus, -1.4 V was used as the deposition potential in the following electrochemical measurement.

Fig. 2b demonstrates the influence of deposition time in a range from 5 s to 90 s on the stripping peak current at the -1.4 V deposition potential. The peak current increased sharply with increasing deposition time, because of the increased amount of Pb²⁺. However, the stripping peak current started to increase slowly after the deposition time of 30 s, possibly due to the surface saturation of the WE. Therefore, 30 s was chosen as the optimal deposition time.

Figure 3: (a) Output current curves from varies concentrations of Pb²⁺. (b) Calibration curve of (a).

Fig. 3a shows the stripping response of the sensor at different Pb²⁺ ion concentrations (5, 10, 20, 50, 100, 200, 400, and 500 ppb). The Pb²⁺ current peak appeared at -0.32 V with respect to the potential of the RE. The corresponding calibration curves exhibited a linear relationship over the concentration range of from 5 ppb to 100 ppb. The calculated sensitivity of the sensor is about 67.9 nA/ppb (Fig.3b). The LOD of the sensor (defined as the concentration which yield a measure peak with signal-to-noise ratio of 3) was calculated to be about 0.3 ppb of Pb²⁺.

Figure 4: Output current peaks from the mixture of Cd^{2+} and Pb^{2+} .

Fig. 4 shows the output curve from the mixture of Cd^{2+} and Pb^{2+} , showing the high selectivity of the sensor. Compared to existing heavy metal ion sensors, the presented sensor offers not only a comparable or better LOD, but also higher compactness and IC compatibility.

CONCLUSION

We report a miniaturized heavy metal ion sensor able to detect sub-ppb-level Pb^{2+} in water. The sensor integrates a microfabricated planar Bi WE, an Au counter electrode and an Ag/AgCl RE into a microfluidic channel to perform ASV measurement of Pb^{2+} . The developed on-chip sensor exhibited a sharp stripping peak current and a low detect limit for Pb^{2+} . It could be used to monitor many other heavy metal ions in industrial and residential water.

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