ELECTROCHEMICAL SENSORS FOR HEAVY METAL DETECTION USING PYROLYTIC CARBON AND GOLD ELECTRODES

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ABSTRACT

This study presents an integrated sensor array utilizing pyrolytic carbon and gold electrodes for sensitive detection of heavy metals (arsenic, copper, lead, and cadmium) in water. By employing glassy carbon electrodes for Pb and Cd detection and gold electrodes for As and Cu, along with Bismuth (Bi) integration to enhance sensitivity, the sensor array achieves impressive selectivity and detection limits of 10 ppb for Pb, 20 ppb for Cd, 10 ppb for As, and 20 ppb for Cu. The research emphasizes comprehensive heavy metal detection under various ion conditions, offering a promising solution for environmental monitoring and health risk assessment.

KEYWORDS

Heavy metal detection, Pyrolytic carbon and gold electrodes array, Water quality, Pollution monitoring

INTRODUCTION

Heavy metal ions such as arsenic (As), copper (Cu), lead (Pb), and cadmium (Cd) pose significant health risks and environmental concerns when present in water sources. Arsenic, a known carcinogen, can lead to various health issues including skin lesions, cardiovascular diseases, and even cancer upon long-term exposure [1]. Copper, while essential in small amounts, can be toxic in higher concentrations, causing gastrointestinal distress, liver and kidney damage, and neurological disorders [2]. Lead is notorious for its neurotoxic effects, especially in children, leading to developmental delays, learning disabilities, and behavioral problems. Cadmium, another carcinogen, can accumulate in the kidneys and liver, causing renal dysfunction and bone damage [3]. Additionally, heavy metals can bioaccumulate in the food chain, posing risks to both aquatic life and human consumers [4], thus necessitating stringent detection and monitoring measures.

Traditional methods for detecting heavy metals in water include atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and colorimetric assays. While these methods offer high sensitivity and accuracy, they often require expensive equipment, skilled personnel, and time-consuming sample preparation procedures. Furthermore, these techniques may not be suitable for on-site or real-time monitoring applications, limiting their utility in rapidly assessing water quality in diverse environmental settings. Additionally, interference from other ions and matrix effects can complicate the analysis, necessitating extensive calibration and validation procedures.

Anodic Stripping Voltammetry (ASV) emerges as a promising electrochemical method for heavy metal detection, offering rapid, sensitive, and selective analysis with minimal sample preparation [5]. ASV involves depositing a metal onto an electrode surface, followed by stripping off the deposited metal ions, allowing for quantitative determination. Its advantages include low detection limits, wide linear range, high sensitivity, and excellent selectivity, making it well-suited for detecting trace levels of heavy metals in complex sample matrices. Moreover, ASV can be easily integrated into sensor platforms, enabling on-site monitoring and real-time analysis of water quality.

This study adopts a novel approach by utilizing a sensor array comprising glassy carbon and gold electrodes for the simultaneous detection of heavy metals via ASV. By employing ASV coupled with specific electrode materials and integration of bismuth (Bi) for enhanced sensitivity, the sensor array demonstrates impressive performance in discerning Pb, Cd, As, and Cu in polluted water samples. The results indicate detection limits of 10 ppb for Pb and As, and 20 ppb for Cd and Cu, showcasing the array's potential for sensitive and selective heavy metal detection in diverse environmental conditions. This innovative approach holds promise for addressing the urgent need for effective monitoring and mitigation of heavy metal contamination in water resources, thereby safeguarding human health and environmental integrity.

EXPERIMENTAL

Materials and Reagents

All materials and reagents utilized in this study were of analytical grade and obtained without prior purification. Sodium acetate, acetic acid, standard solutions of 1000 ppm for lead (Pb), arsenic (As), cadmium (Cd), copper (Cu), and bismuth (Bi) were sourced from Sigma Alrich. KMPR 1035 photoresist was purchased from Kayaku Advanced Materials, Inc. Deionized water was employed for the preparation of all solutions.

Device Fabrication

Glassy carbon electrodes were fabricated using techniques rooted in Carbon Microelectromechanical Systems (C-MEMS). Figure 1A depicts the microfabrication process, while Figure 1B illustrates fabricated the sensor array device following our previously reported fabrication [5, 6, 7].

Briefly, The working and counter electrodes were constructed from patterned KMPR photoresist pyrolyzed at 1,100 °C. Negative photoresist was initially spin-coated onto a silicon wafer at 3,000 rpm, resulting in a thickness of 38 µm. Subsequently, photolithography was employed to pattern the photoresist, yielding the desired electrode structures. The wafer with phot oresist was then subjected to pyrolysis at 1,100 °C for 5 hours under a continuous flow of a 5% hydrogen and 95% argon gas mixture. Once the pyrolyzed carbon electrodes were fabricated, 100 nm of gold film is deposited with 30 nm of chromium as the seed layer via an electron-beam evaporator. The gold film was further patterned via photolithography to achieve the desired electrode design.

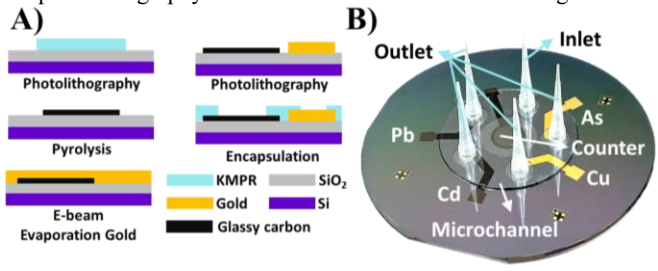

Figure 1: A) Schematic diagram of the fabrication process and B) optical image of the heavy metal sensor array

Measurement Setup

Different concentrations of heavy metal ion samples were prepared by diluting standard solutions of Pb, As, Cd, Cu, and Bi using a 0.1 M acetic acid buffer, with all measurements conducted in the same buffer solution maintaining a stable pH value of 4.5.

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Utilizing an electrochemical station (N Series Potentiostat/Galvanostat Instruments, Metrohm Autolab), the ASV method was employed. Glassy carbon electrodes were subjected to a negative deposition potential of -1 V for 300 seconds for Pb and Cd detection, while gold electrodes underwent a -0.5 V deposition potential for 300 seconds for As and Cu detection. Following the deposition, a square-wave voltammetry scan from -1.2 V to -0.1 V was applied to the working electrode for stripping, with parameters including a scan frequency of 60 Hz, a potential step size of 20 mV, and a modulation amplitude of 50 mV.

RESULTS AND DISCUSSION

Measurement optimization

The glassy carbon electrodes were initially utilized to optimize the measurement conditions for Pb. Bi was employed to enhance the stripping current peak of Pb by forming multi-component Bi alloys with heavy metals [5]. Figure 2A illustrates the stripping current of the Pb sensor under a constant concentration of 20 ppb Pb, with varying Bi concentrations ranging from 25 ppb to 150 ppb. Figure 2B demonstrates the stripping peak height for Pb under different Bi concentrations. It was observed that the stripping peak height of Pb initially increased and reached its maximum at a Bi concentration of 100 ppb. However, as the Bi concentration continued to increase, the peak height of Pb declined. This phenomenon resulted from the competitive interaction between Bi and Pb during the accumulation stage at higher Bi concentration. To optimize Pb detection, a Bi concentration of 100 ppb was selected.

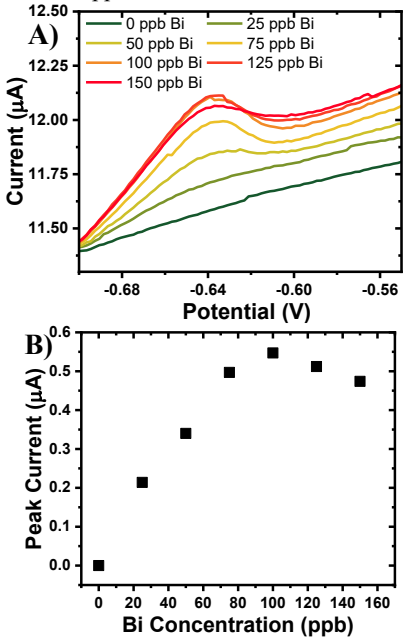

Figure 2: A) Stripping voltammograms of Pb with increasing Bi concentrations from 25 ppb to 150 ppb with constant Pb concentration of 25 ppb. B) Peak current height of Pb with increasing Bi concentrations.

Lead Measurement

The glassy carbon electrodes were employed to measure Pb in a 0.1 M acetic acid buffer solution. The concentration of Bi was held constant at 100 ppb, resulting in the highest current peak height of Pb. Figure 3A illustrates the stripping current of the Pb sensor with concentrations ranging from 5 ppb to 100 ppb. As the concentration of Pb increased, the Pb peak height exhibited a linear increase, as depicted in Figure 3B. Additionally, the limit of detection was established to be 10 ppb.

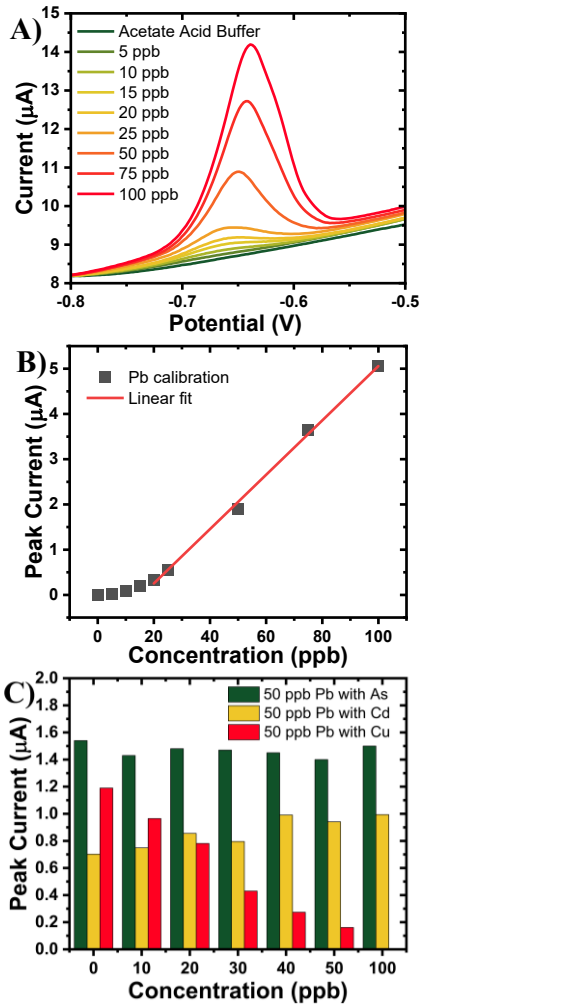

Figure 3: A) Stripping voltammograms of Pb with increasing concentrations from 5 ppb to 100 ppb with constant Bi concentration of 100 ppb. B) Calibration curve of Pb measurement. C) Peak current height of Pb with increasing As, Cd, and Cu concentrations.

To ensure accurate detection of Pb in a complex environment, measurements were replicated with various interfering heavy metal ions under identical conditions. The concentration of Pb was held constant at 50 ppb, while different heavy metal ions, including As, Cd, and Cu, were introduced at varying concentrations. As depicted in Figure 3C, the peak current height of Pb remained consistent as the As concentration increased from 10 ppb to 100 ppb, indicating no co-deposition of As with Pb during the accumulation step. The peak current height of Pb remained constant with increasing Cd concentrations from 10 ppb to 100 ppb. Indicating that Cd did not significantly influence the Pb detection. Furthermore, the peak height of Pb was notably influenced by the presence of Cu due to its lower redox potential. During the accumulation step, more Cu ions were reduced, leading to a decrease in the oxidation peak when measuring Pb. To address this interference, a Cu sensor was integrated with the Pb sensor.

Cadmium Measurement

The glassy carbon electrodes were also used to measure Cd in a 0.1 M acetic acid buffer solution. A constant concentration of Bi of 100 ppb was maintained due to its role in Pb detection. Figure 4A illustrates the stripping current of the Cd sensor with increasing

concentrations from 5 ppb to 100 ppb. As the concentration of Cd increased, the Pb peak height increased linearly, and a limit of detection of 20 ppb was obtained, as shown in Figure 4B.

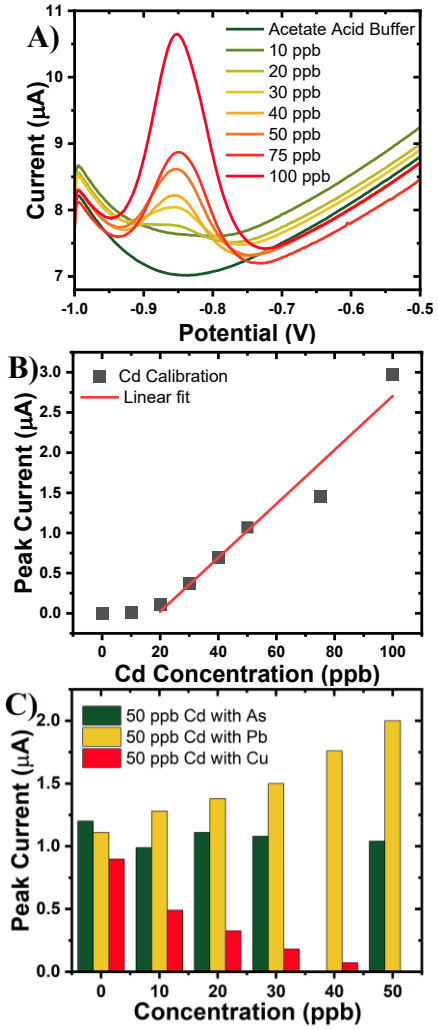

Figure 4: A) Stripping voltammograms of Cd with increasing concentrations from 5 ppb to 100 ppb with constant Bi concentration of 100 ppb. B) Calibration curve of Cd measurement. C) Peak current height of Cd with increasing As, Cd, and Cu concentrations.

Interferences from other common heavy metal ions were investigated, as depicted in Figure 4C. Under identical measurement conditions, the concentration of Cd was held constant at 50 ppb, while the concentrations of other interfering ions, including As, Pb, and Cu, were varied from 10 ppb to 50 ppb. As illustrated in Figure 4C, the peak current height of Cd remained relatively constant with minor fluctuations as the As concentration increased, indicating no significant amount of As ions were reduced over the glassy carbon electrode surface. Similar to Pb detection, Cd and Pb may co-deposit. When the concentration of Cd was fixed, increasing Pb concentration enhanced the peak current height of the Cd sensor, attributed to the enhanced stripping of Cd in the presence of Pb. Furthermore, it was observed that Cu significantly reduced the peak current height of Cd. Due to the lower redox potential of Cu, it could be easily reduced, competing with the reduction of Cd, resulting in a reduced peak current height of Cd. When the concentration of Cu increased to 50 ppb, the peak height of Cd approached zero. This is also due to the reduction of Cu during the accumulation step, leading to a decrease in the oxidation peak of Cd.

Arsenic Measurement

Due to the higher carrier mobility of gold electrode, it was expected to exhibit a lower detection limit. Since the redox potential of As is higher than Pb or Cd, a less negative potential of -0.5 V was applied. Moreover, hydrogen evolution was not observed at such potential. Therefore, to achieve a lower detection limit, gold electrodes were used for As and Cu detection. In the same 0.1 M acetic acid buffer solution, the concentration of As ranged from 5 ppb to 100 ppb, and ASV was conducted. As depicted in Figure 5A, the stripping current increased uniformly with the increasing As concentration. The limit of detection was determined to be 10 ppb, as illustrated in Figure 5B.

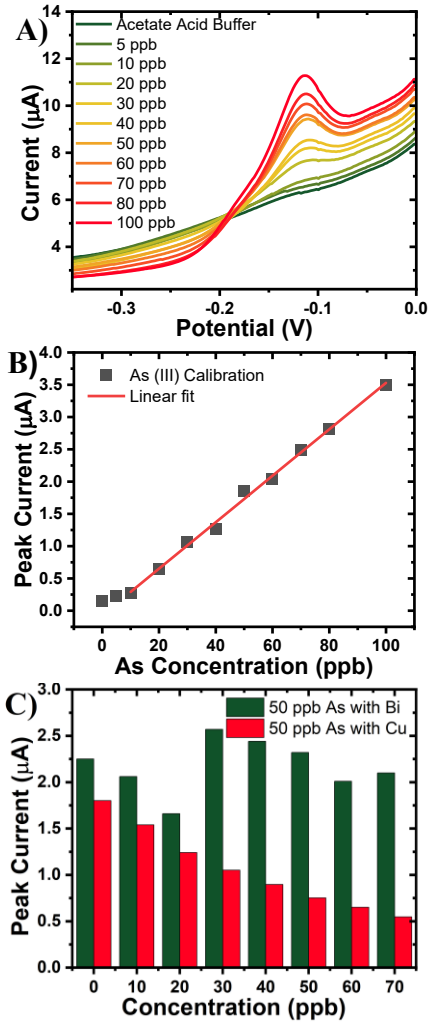

Figure 5: A) Stripping voltammograms of As with increasing concentrations from 5 ppb to 100 ppb. B) Calibration curve of As measurement. C) Peak current height of As with increasing Bi and Cu concentrations.

When using gold electrodes for measurement, a deposition potential of -0.5 V was applied. Under such potential, neither Pb nor Cd undergo electrochemical reductions. Therefore, only Bi and Cu were tested for interference effects. As depicted in Figure 5C, the concentration of As was fixed at 50 ppb, while the concentrations of Bi and Cu varied from 10 to 70 ppb. As the Bi concentration increased, the peak current height of As exhibited a high degree of fluctuation when the Bi concentration was below 50 ppb. However,

the magnitude of the response stabilized when the Bi concentration exceeded 50 ppb. Since the measurement of Pb and Cd requires a constant Bi level of 100 ppb, the As response was expected to remain stable during measurement. In contrast, it was observed that Cu significantly reduced the peak current height of As due to its lower redox potential.

Copper Measurement

Cu exerts a significant influence on other heavy metal detections due to its lower redox potential. To calibrate the effect of Cu, a Cu sensor was integrated with the sensor array, and gold electrodes were employed for detection. In a 0.1 M acetic acid buffer solution, the concentration of Cu varied from 5 ppb to 90 ppb. As depicted in Figure 6A, the stripping current increased with the increasing concentration of Cu. The limit of detection was determined to be 20 ppb, as illustrated in Figure 6B.

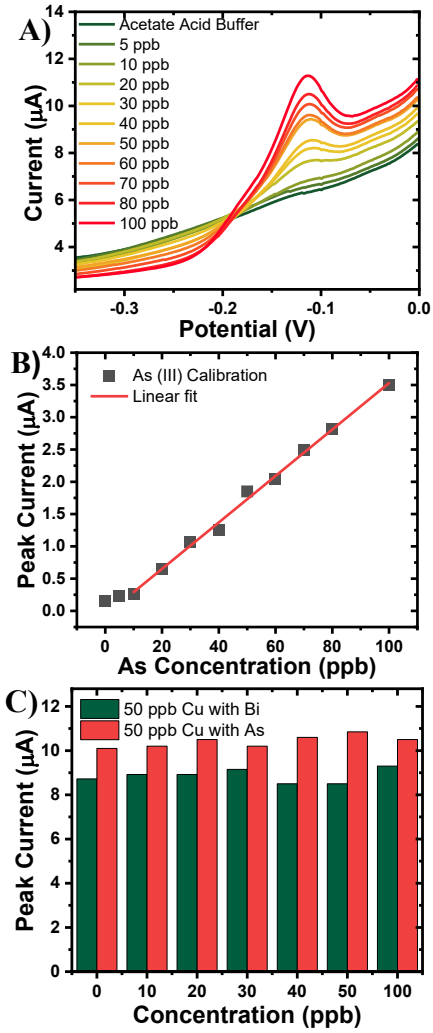

Figure 6: A) Stripping voltammograms of As with increasing concentrations from 5 ppb to 100 ppb. B) Calibration curve of As measurement. C) Peak current height of As with increasing Bi and Cu concentrations.

The interference effect was assessed by measuring the peak current of Cu in the presence of other heavy metal ions. Due to the low potential applied to the gold electrode, the Pb and Cd ions will not undergo reduction. Hence, only Bi and As were investigated. The peak current height of Cu showed no reduction when Bi or As were added, indicating stable responses in Cu measurements. Therefore, the Cu sensor was integrated with the other heavy metal sensors to calibrate the effect of Cu, aiming to achieve higher sensing accuracy.

CONCLUSION

In conclusion, the study employs glassy carbon electrodes for lead (Pb) and cadmium (Cd) detection and gold electrodes for arsenic (As) and copper (Cu) detection in an electrochemical sensor array via anodic stripping voltammetry (ASV). Moreover, bismuth (Bi) is integrated to enhance sensitivity of Pb and Cd sensor. Interference tests demonstrate stable peak current heights for individual metals, showcasing the sensor's ability to discern Pb, Cd, As, and Cu amidst each other. Detection limits are determined as 10 ppb for Pb, 20 ppb for Cd, 10 ppb for As, and 20 ppb for Cu. The sensor array proves promising for sensitive heavy metal detection in diverse environments.

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