

DISPOSABLE COPPER-BASED ELECTROCHEMICAL MICROSENSOR FOR ANALYSIS OF LEAD IN ENVIRONMENTAL SAMPLES

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ABSTRACT

In this work, we report on rapid analysis of lead (Pb) of surface river water using low-cost, disposable copper-based electrochemical sensors. Conventionally, electrochemistry is performed using carbon or gold/platinum electrodes, which can be difficult or expensive to microfabricate. Our sensor features a new, low-cost electrode material—copper—which offers simple fabrication and competitive performance in electrochemical detection. Measurements of Pb using anodic stripping voltammetry (ASV) show limit of detection (LOD) of 21 nM (4.4 ppb) and stable response in environmental samples with no need of complex pretreatment.

KEYWORDS

Copper, electrochemical sensor, lead, disposable sensor, environmental sample

INTRODUCTION

Lead is a highly poisonous metal, as it affects almost every human organ, such as kidney, nervous system and immune system. It could permanently reduce the cognitive capacity of children. The sources of Pb exposure include mining, smelting, lead-containing gasoline and lead paint. It can enter the body through hand-to-mouth contact or through contaminated food or water. The high toxicity and common occurrence requires carefully monitoring of Pb. The guideline value for the safe level of Pb in drinking water is 10 ppb (48 nM) [1].

Compared to standard methods, such as atomic absorption spectroscopy (AAS) or inductively coupled plasma mass spectroscopy (ICP-MS), electrochemical techniques for heavy metal detection require simpler instruments and provide possibility to miniaturize. In particular, anodic stripping voltammetry (ASV) is a commonly approach for the detection of heavy metals. The limit of detection (LOD) of this technique can be as low as 10^{-12} M, which is sufficient for most trace metal detection needs.

In addition to the conventional bulk carbon-based or gold/platinum electrodes for electrochemical detection, several microsensors using different materials like paper and silver [2,3] have been reported for Pb detection with LOD of less than 1 ppb in buffer and sample volume of 100 μ L or less. Our group also reported [4] a gold-based microsensor with bismuth working electrode for multi-metal detection including Pb. However, they did not report the sensors' performance in environmental samples.

In this paper, we will present a copper (Cu)-based sensor with Cu working and auxiliary and Cu/CuCl₂ reference electrodes. Cu is a new, low-cost electrode material which offers simple fabrication and competitive performance in electrochemical detection. Our previous work [5] has demonstrated the electrochemical performance of Cu-based sensors by ASV of zinc. This paper reports the Pb analysis in buffer and environmental sample. By optimizing experimental parameters, the Cu-based sensor exhibited low LOD for Pb, measured at 21 nM (4.4 ppb) of ASV in acetate buffer, good sensitivity of more than 3.4 μ A/ μ M, and good linearity in the range below 10 μ M. ASV of Pb also provides stable response in environmental samples with no need of complex pretreatment and demonstrate there is no Pb contamination in the sample.

EXPERIMENTAL

The electrochemical sensor was fabricated using a combination of lithographic and deposition techniques. Metal layers of 20 nm titanium (Ti) /200 nm Cu were evaporated on glass slides cleaned by piranha etching. Three electrode patterns with contact pads were formed using photolithography and wet etching. A new reference electrode, Cu/CuCl₂, was simply fabricated by chloridizing Cu with 69 μ A for 30s. The electrodes layout is shown in the photograph of a completed sensor in Figure 1b.

A polymer well was fabricated in polydimethylsiloxane (PDMS) using standard soft lithography methods. It was bonded to glass substrates containing electrode patterns using plasma discharge. A platform was fabricated to simplify the connection between sensors and potentiostat. An edge board connector and a mini USB port were soldered and

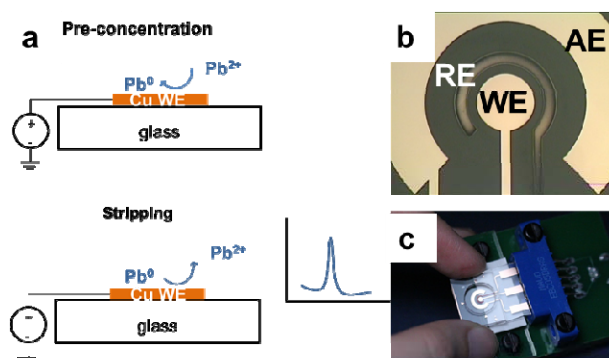


Figure 1a. Illustration of anodic stripping voltammetry for Pb. b. Image of three electrodes. c. Photograph of the sensor with an interface connecting to potentiostat.

connected on a PCB board. To perform electrochemical experiments, as shown in Figure 1c, the sensor was inserted into the edge board connector, and connected to potentiostat (WaveNow, Pine Instrument) using a mini USB cable.

RESULTS & DISCUSSION

The sensor of this work is the first sensor using Cu as the material for both working and auxiliary electrodes, with an integrated Cu/CuCl₂ reference electrode. Cu is not common material for electrochemical sensors since it is easily oxidized. Our previous work [5] has demonstrated the electrochemical performance of Cu-based sensors. Regarding to the stability of reference electrode and auxiliary electrode, the sensor is sufficiently robust for ASV with pre-concentration time of 600 s, which is long enough for most stripping analysis as disposable sensors. Cu working electrode provides the potential window from 0 V to -1 V (vs. Cu/CuCl₂ reference electrode) in acetate buffer, which brackets electronegative metals like Zn, Cd and Pb.

Cyclic voltammetry (Figure 2) shows negative range of potential window for Cu-based sensor and the position of Pb stripping peak. Compared to our previous sensor with bismuth working electrode, Pb peak shifts from -700 mV to -300 mV [4]. The second stripping peak at -500 mV is possibly a separate Pb peak due to high concentration, at which the Pb has been deposit on a thin layer of Pb instead of Cu working electrode. The similar phenomena is also observed in ASV.

To construct a calibration curve and determine the LOD of Cu-based sensors in acetate buffer for Pb detection, experimental parameters were optimized for sensors by performing ASV in 10 μ M Pb in acetate buffer, 0.1 M, 100 μ L. The parameters include pH of acetate buffer, pre-concentration potential, waveform parameters and duration of pre-concentration. Initial parameters were set as following: pre-concentration potential -0.7 V, duration 300 s, amplitude 25 mV, period 70 ms, increment 4 mV. For each parameter, three experiments were performed using three devices, providing the standard deviation indicated as error bars in Figure 3. By comparing the peak currents and errors, pH 5.5, -0.8 V, 50 ms, 50 mV, 8 mV and 300 s were

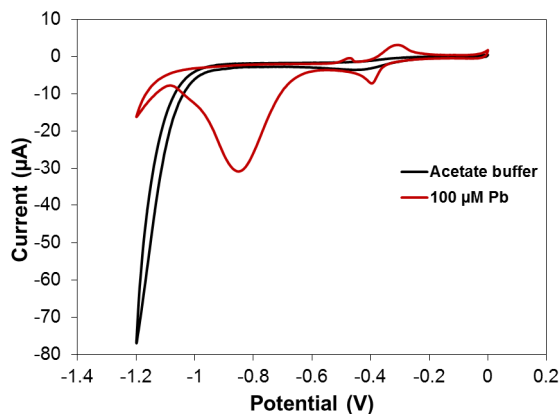


Figure 2. Cyclic voltammetry of acetate buffer (0.1 M, pH 5.5) and 100 μ M Pb. Scan rate 100mV.

selected sequentially for following experiments. As shown in Figure 3d & 3e, by increasing the amplitude and increment of square wave, the peak current kept increasing. However, the purpose of optimization is not only for large peak current which represents high sensitivity, but also for low LOD. Therefore, another characteristic quantity of peak, half height width, was also considered as a factor for selecting proper parameters. The larger half height width indicates the peak losing its resolution while the value of peak going up, which is bad for LOD. So, instead of extreme parameters for the square wave, we selected 50 mV and 8 mV for amplitude and increment, respectively. Noted that these parameters are not independent, a different order of how we did experiments and selected each parameter could lead to a different set of parameters, so the outcome of these experiments is to improve not maximize the response of the sensors. By optimizing these parameters, we obtained signals amplified by 4.4 times, from 8 μ A (pH 4.65, -0.7 V, 70 ms, 25 mV, 4 mV and 300 s) to 35 μ A (pH 5.5, -0.8 V, 50 ms, 50 mV, 8 mV and 300 s).

After optimizing all parameters, calibration curves were constructed by performing ASV in 0.025-10 μ M Pb of 100 μ L in 0.1 M acetate buffer, as shown in Figure 4a, using selected parameters. When the Pb concentration is lower than 10 μ M, ASV show a single stripping peak at -0.3 V. While when the Pb concentration is as high as 10

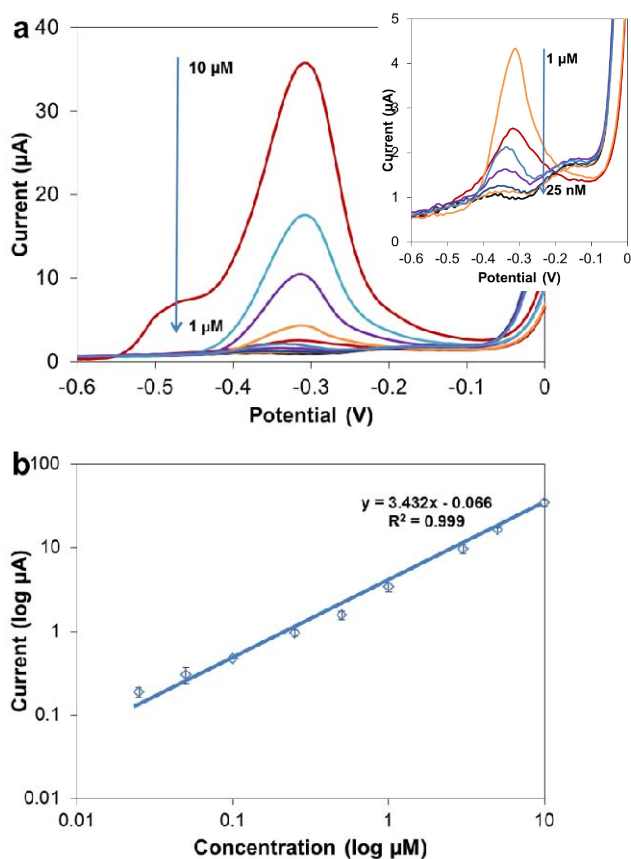


Figure 4 a. Anodic stripping voltammetry of Pb in acetate buffer (0.1 M, pH 5.5), 100 μ L. Pre-concentration potential -0.8 V, duration 300 s, amplitude 50 mV, period 50 ms, increment 8 mV. b. Calibration curve for Pb in buffer.

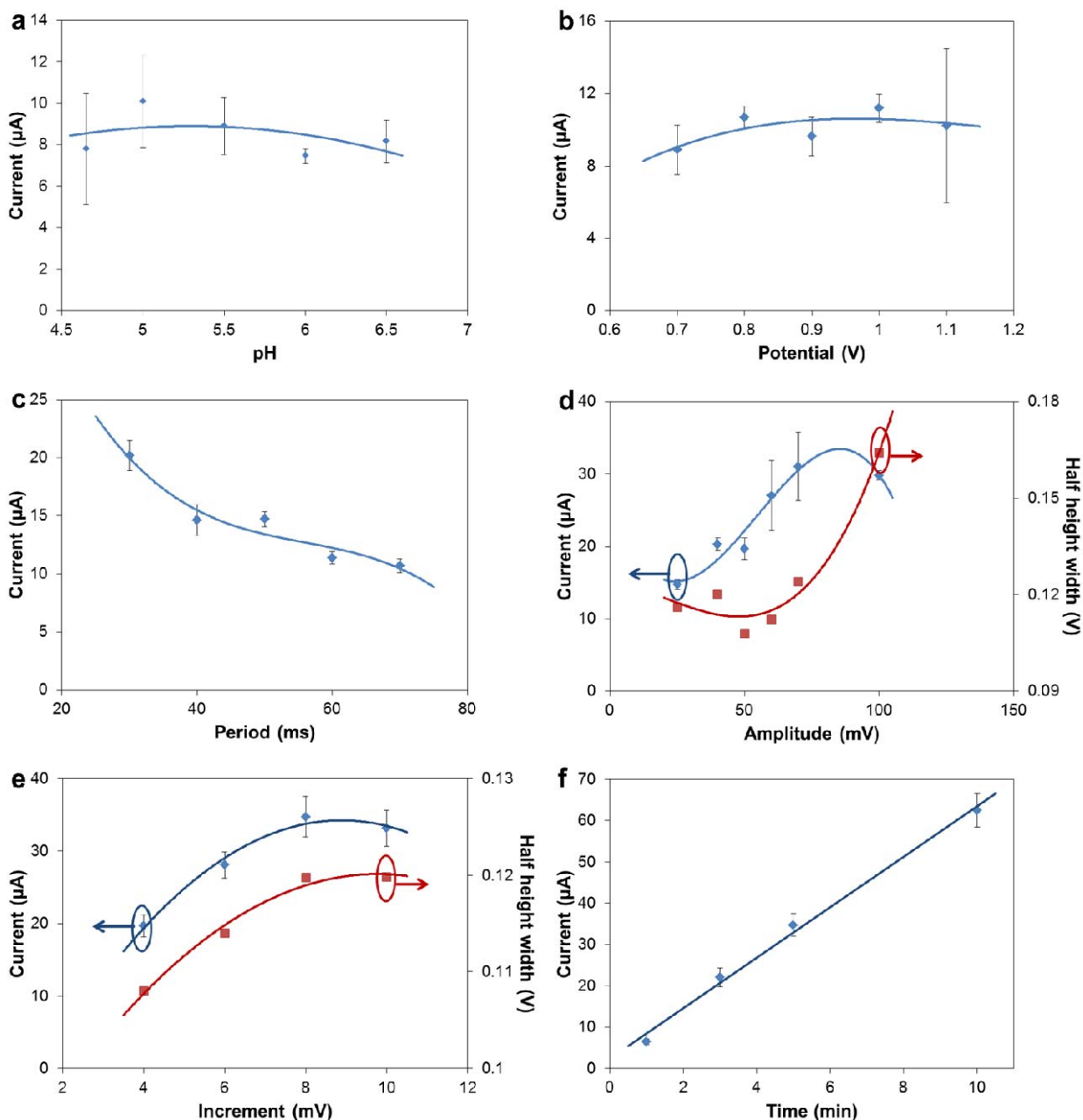


Figure 3. Optimization of experimental parameters: a. pH of acetate buffer, b. pre-concentration potential, c. period, d. amplitude, e. increment, f. duration of pre-concentration. ASV of Pb was performed in acetate buffer, 0.1 M, 100 μ l. Initial parameters: Pre-concentration potential -0.7 V, duration 300 s, amplitude 25 mV, period 70 ms, increment 4 mV. pH 5.5, -0.8V, 50 ms, 50 mV, 8 mV and 300 s was selected sequentially for following experiments.

μ M, a small shoulder starts to show up at -0.5 V. The possible reason is that Pb starts to be deposit on top of Pb instead of Cu, which requires lower potential to strip off. The calibration curve, shown in Figure 4b, indicates the sensitivity of Cu-based sensor for Pb in acetate buffer is 3.432 μ A/ μ M, with good linearity ($R^2=0.999$). Seven measurements of 25 nM Pb were performed for calculating the LOD, which was 21nM or 4.4 ppb (3σ /slope method, $n=7$). This LOD is low enough to determine whether the Pb in environmental sample exceed the safe level in drinking water.

To demonstrate the capability of the sensor to work in environmental matrices, we measured Pb in water

samples from the Ohio River (Ohio, USA). Sample pH was adjusted to 5.5 using acetic acid and diluted by acetate buffer (0.1 M, pH 5.5) by 2 \times . Standard addition approach was used to determine Pb concentration in the sample. Figure 5a shows the ASV of the original sample and spiked with additional Pb, using the same parameters as in buffer. Pb peaks show up at the same position, -0.3 V, as in buffer. Standard addition curve (Figure 4b) shows the linear response for 25-500 ppb additions of Pb with sensitivity of 6.21 μ A/ μ M which is even superior to that of the acetate buffer. One possible reason is larger ion strength of the sample due to its complex compositions. Since there is no Pb peak in the ASV of

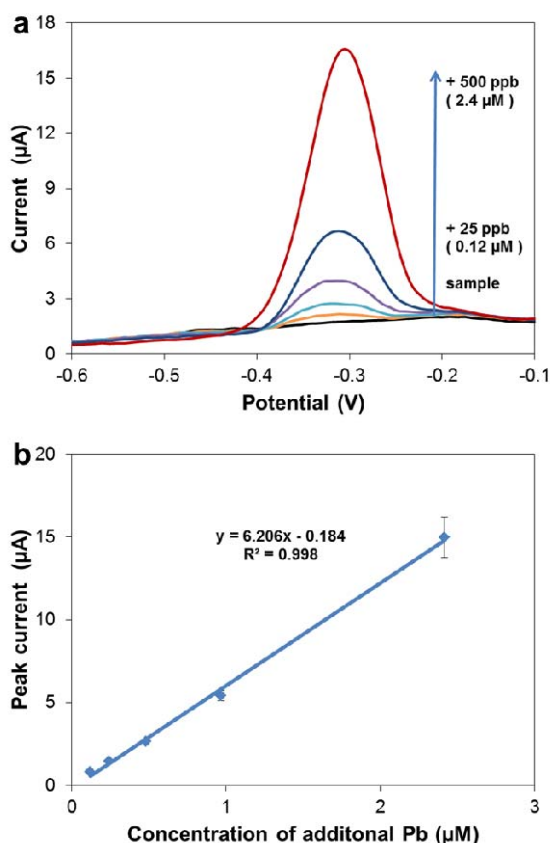


Figure 5. a. Anodic stripping voltammetry of river water sample and with additional Pb, 100 µL. Parameters are the same as in buffer. b. Standard addition curve for Pb in river water sample.

the original sample, the Pb level in the sample from the Ohio River (Cincinnati, OH) is less than 2 (dilution factor) \times LOD, 8.8ppb, which is below the safe level in drinking water. The same sample was also delivered to another lab and tested by AAS. The AAS result confirmed that there was no Pb contamination in the sample.

CONCLUSIONS

We demonstrated a new electrochemical sensor concept for rapid analysis of lead in river water. The result showed no lead contamination in the sample and was confirmed by AAS. The test takes 5 min and does not require sample pretreatment. The simplicity and capability of this method make it possible to monitor Pb levels on-site and continuously. The disposable copper-based sensors are easy to fabricate, are low-cost, and show competitive electrochemical performance for Pb and other metals in biological or environmental samples [5]. These features are highly desirable for point-of-care applications.

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