Ultra-sensitive Electrochemical Determination of Mercury Ions Based on the Dithizone Modified Electrode

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Mercury-ion pollution in water is very dangerous to human health and ecological environments. It is necessary to propose a simple, fast and low-cost testing method for mercury-ion detection. Cold atomic spectrophotometers are often used for the detection of mercury ions, but because the instruments are expensive and cumbersome to operate, the method is only suitable for laboratories. In this work, we propose a simple electrochemical method for the determination of mercury ions based on a dithizone-modified glassy carbon electrode. The dithizone modification can significantly enhance the sensing performance of the electrode. Under optimized conditions, the proposed electrochemical sensor can linearly detect Hg(II) between 0.1 and 100 μg/L with a low detection limit of 17 ng/L.

1. INTRODUCTION

The water environment mainly includes rivers, lakes, reservoirs, oceans and other water bodies, such as industrial water, discharge water and drinking water. The basic chemical composition and content of natural water represent its original physical and chemical properties in different natural environmental cycles [1–5]. The water environment is one of the basic elements of the overall environment and an important place for the survival and development of human society. It is also the most disturbed and destroyed area by human beings. The pollution and destruction of the water environment has become one of the main environmental problems in the world. In recent years, with the rapid development of industry, agriculture and economy, the pollution of heavy metals in all kinds of water environments has become increasingly serious [6–10].

Many tourist attractions contain water areas, but there are no sewage treatment systems. Tourists produce a large amount of household garbage, such as sewage, which is directly released into the lake or surrounding grassland. Sewage accompanied by many detergents and other chemical components can move onto soil and permeate underground [11–16]. This release of sewage can directly affect the quality of water because groundwater is connected; thus, part of the sewage will seep into the water, leading to the decline of water quality and causing damage to the ecological environment. Among the various pollutants, heavy metal ions can significantly affect human health. Heavy metals are one of the most dangerous pollutants, and they often accumulate in the body for a long time because they cannot be degraded. Heavy metals are deposited in the human body through the food chain, causing many diseases and even cancer; furthermore, the damage can be passed on to the next generation [17–23].

At present, there are many related technologies for the detection of heavy metal ions in the water environment, such as flame atomic absorption spectrometry [24–26], a quartz crystal microbalance chemical sensor [27–30], spectrophotometer detection [31,32] and PAR modified colorimetric fibre detection [33–36]. However, many of the results of these studies are confined to the laboratory and are difficult to apply in the real environment. Therefore, we chose electrochemical sensors as the main research object of this paper. These sensors have the advantages of easy miniaturization, little influence by environmental conditions, good sensitivity and low detection limit, which make them very suitable for heavy metal detection [37–42].

Electroanalytical chemistry is recognized as a fast, sensitive and accurate method for trace analysis when analysing chemical composition [43–47]. The detection concentration of metal ions can reach the pM level. In addition, electroanalytical chemistry is very useful under harsh environmental conditions. The surface and interface electroanalytical chemistry developed in the past ten years has put electroanalytical chemistry into the field of high technology.

Dithizone is widely used in analytical chemistry. Dithizone is used to form a coloured complex with divalent metal ions such as lead, gold, mercury, and zinc. The complex can be dissolved in organic solvents, then the metal ions can be extracted from the aqueous phase to the organic phase and separated from the mother liquor to achieve separation and enrichment [48–54].

The relation between colour depth and metal ion concentration is in accordance with Beer's law. The dithizone method for the determination of trace metal ions has the advantages of sensitivity, accuracy and no need for large instruments. Therefore, it has been the standard method for the determination of lead, mercury and zinc in food and the environment. There are relatively few studies on the use of dithizone to determine mercury because standard mercury determination requires a cold atomic fluorescence spectrophotometer. However, atomic fluorescence spectrophotometry has higher requirements for analysis conditions and environment. Therefore, an electrochemical method is used to determine mercury in this work, and the working electrode is modified with dithizone to improve the sensitivity and obtain a lower detection limit.

2. EXPERIMENTAL

All chemicals were purchased from Aladdin Biotechnology Co., Ltd. (Shanghai, China) in analytical grade without further purification.

The glassy carbon electrode (GCE) was first polished with metallographic sandpaper and then polished to a mirror-like surface with 1 μm and 0.3 μm Al_2O_3 polishing powder successively. After each polishing, the surface was washed twice with water and transferred to an ultrasonic water bath for cleaning before being dried naturally. After thorough cleaning, the GCE was activated by cyclic voltammetry in 0.5 M H_2SO_4 solution in the scan range of -0.3 V to 1.3 V, and repeated scans were conducted until the output electrochemical signal was stable. Finally, a CV scan was carried out in 0.1 M potassium ferricyanide solution to test the electrode performance. The potential difference between the peak and reduction peak should be less than 0.08 V. All voltammetric scans were performed by a CHI660D electrochemical workstation (Shanghai Chenhua Instrument Company, China).

For dithizone modification, the pre-treated GCE was dried naturally. Then, 3 μL of 1 g/L dithizone solution was dropped on the GCE surface and dried naturally (denoted as D/GCE).

For mercury-ion determination, the modified D/GCE was immersed into 0.1 M ammonia-NH_4Cl buffer solution containing a certain concentration of Hg(II) at pH 9.5. Under a controlled stirring speed, the electrode system was converted to 0.1 M hydrochloric acid solution after 5 min at a potential of -0.4 V. Then, stripping voltammetry was performed for recording Hg(II).

3. RESULTS AND DISCUSSION

The CV activation of the electrode after pretreatment is shown in Figure 1A. After the activation of the electrode, there are no other metal ions on the surface. Moreover, a layer consisting of an activated layer bonded with a light base and shuttle base will be formed on the surface of the GCE, which is conducive to the bonding of heavy metals and improves the sensitivity of the determination.

The GCE activation can be illustrated by observing a cyclic voltammetric scan towards potassium ferricyanide. The electrochemical characteristics of the electrode before and after electrode treatment are shown in Figure 1B. It is obvious that the redox of GCE without activation treatment has a wider peak shape and a smaller peak current. In contrast, the peak shape of the activated electrode was significantly increased, and the difference between the oxidation peak and reduction peak potential was significantly narrowed compared to that of the un-activated GCE, which proved that the surface activity of the GCE after activation treatment was greatly enhanced. The above results could be due to the electron transfer channels and rate of the sensor being affected by the number of modified electrode materials [55]. The results indicate that H_2SO_4 solution can remove impurities on the electrode surface and improve the electrode performance.
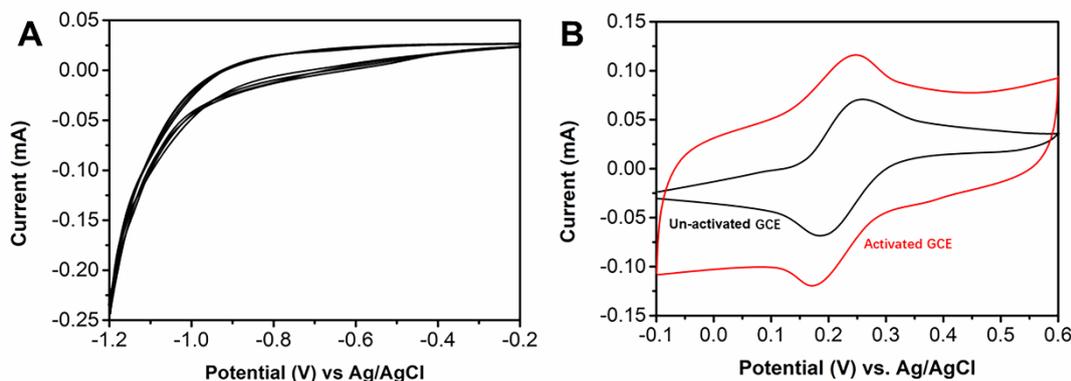
Figure 1. (A) CVs of activated GCE in 0.5 M H_2SO_4. (B) CVs of un-activated and activated GCE in 1 M potassium ferricyanide solution.

Figure 2 shows the stripping voltammetric curves of the bare GCE and D/GCE. Mercury is only electrochemically bonded on the bare GCE, with low enrichment efficiency and a weak voltammetric response. Under the same conditions, mercury on the GCE modified by dithizone not only electrochemically bonds but also chemically bonds, and the two bonds promote each other, which greatly improves the enrichment efficiency and thus produces a sensitive anode dissolution peak. In addition, dithizone complexes have good conductivity and a high concentration of defects produced during the non-equilibrium process, which make them have better electrocatalytic activity [56–60]. It was concluded that the sensitivity of Hg(II) determination could be improved after dithizone modification.
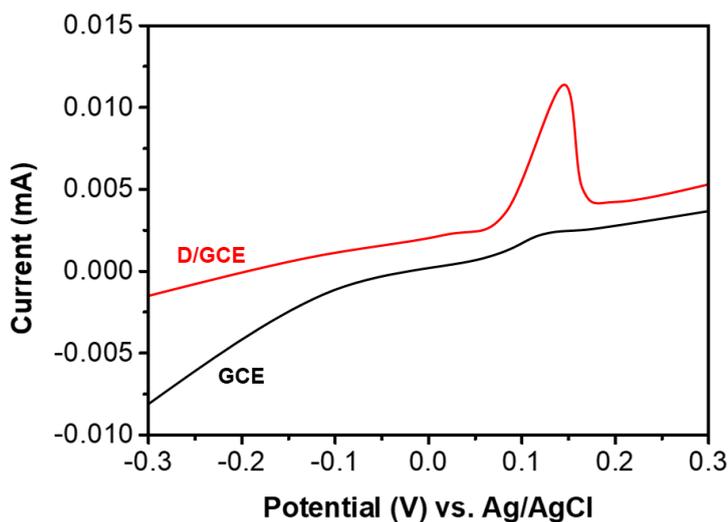

Figure 2. Differential pulse stripping voltammetric curves of Hg(II) with the bare GCE and D/GCE electrodes.

Classic mercury-ion detection devices have the advantages of high sensitivity, good reproducibility, and high accuracy, with a wide range of hydrogen evolution potential, and the possibility of forming an amalgam to obtain a clean surface. However, the voltammetry established for mercury electrodes is limited due to the toxicity of mercury [61]. Accumulation is an important parameter in stripping voltammetry. By comparing the accumulation effects under different potentials, it was found

that when the accumulation potential was -0.40 V, the peak current was the largest. Under the accumulation potential of -0.4 V, the optimal accumulation time for mercury ion determination was studied (Figure 3A). The stripping peak current of mercury ions increases linearly with increasing accumulation time and then increases slowly after reaching the adsorption equilibrium. When the accumulation time is greater than 7 min, the peak current value reaches a maximum and is stable, indicating that the electrode surface adsorption has reached equilibrium. Although the accumulation time can significantly improve the sensitivity of determination, the experimental process time is also critical for the application. In the determination of low-concentration mercury ions, a longer accumulation time can be selected, and 5 min is the optimal accumulation time in this experiment.
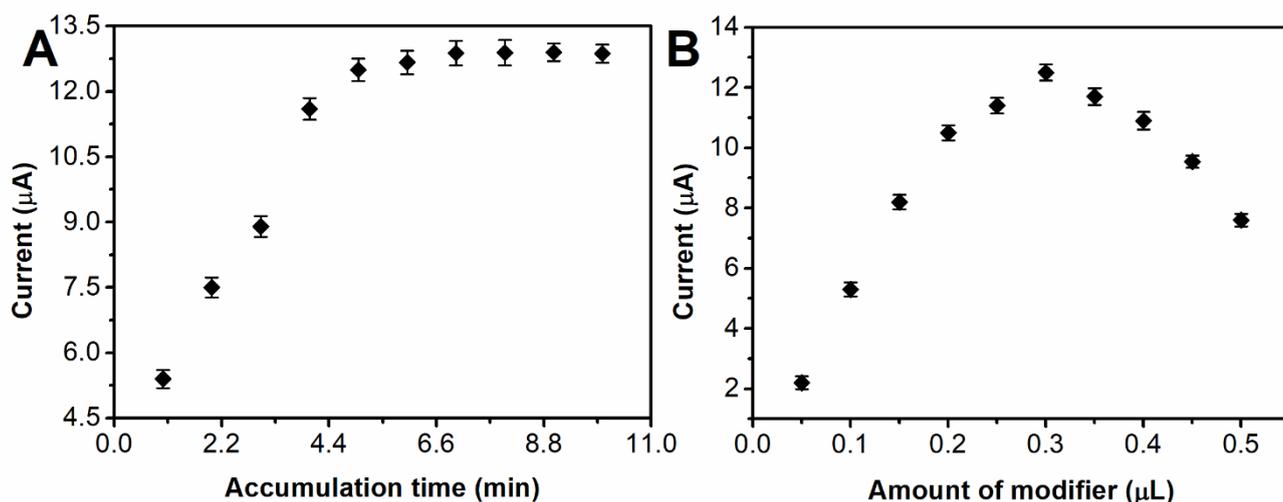

Figure 3. (A) Effect of the accumulation time on the differential pulse stripping voltammetric scans. (B) Effect of the amount of modifier in the differential pulse stripping voltammetric scans.
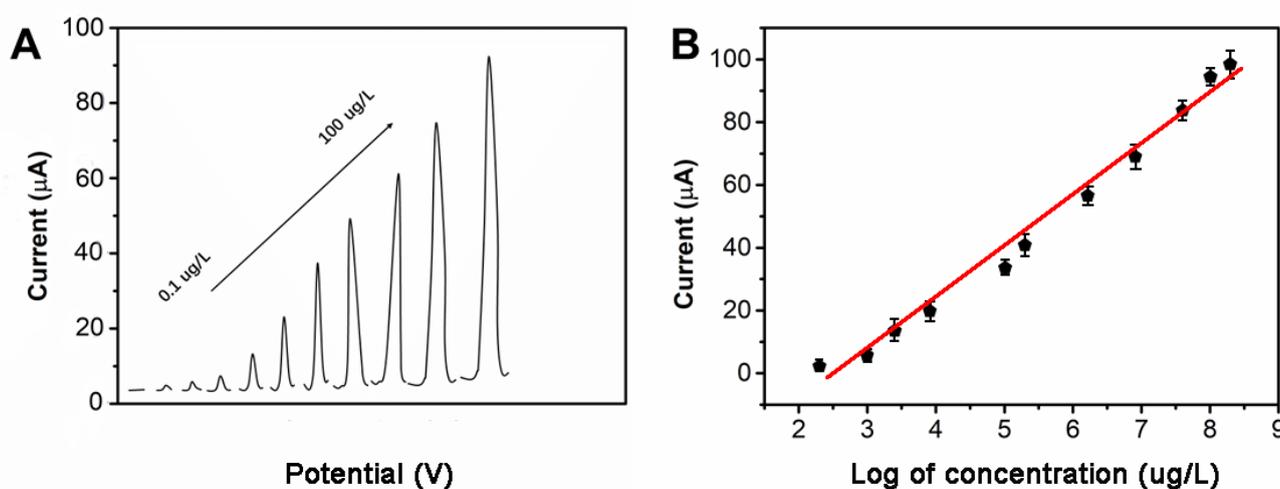

Figure 4. (A) Differential pulse stripping voltammetric profiles of the D/GCE towards different concentrations of Hg(II). (B) Plots of current responses vs. concentrations of Hg(II).

Table 1. Comparison of Hg(II) determination with different electrochemical sensor methods that have been reported.

Electrode	Method	Detection range	Limit of detection	Reference
Bismuth modified exfoliated graphite electrode	DPV	-	270 ng/L	[62]
Nanoporous gold nanoparticles modified indium tin oxide electrode	DPV	0.1 to 10 µg/L	0.03 µg/L	[63]
Polystyrene sulfonate-NiO-carbon nanopowder composite modified SPE	DPV	0.05 to 2.0 µg/L	21 ng/L	[64]
D/GCE	DPV	0.1 to 100 µg/L	17 ng/L	This work

The amount of modifier is also a critical factor in the sensing performance. Figure 3B shows the effect of the amount of modifier in the stripping voltammetric scans. The peak current of Hg(II) increased when the amount of modifier increased from 0.05 µL to 3 µL. However, the peak current decreased when the modifier exceeded 3 µL. This result could be ascribed to a thick surface modification film blocking the mass transfer diffusion of Hg ions in solution to the inner surface of the electrode. At the same time, it prevented the electron exchange between the ion and the working electrode, leading to a decrease in the peak current. Therefore, 3 µL of modifier was selected in this work.

The analytical performance of the D/GCE towards different concentrations of Hg(II) was further examined. Figure 4A shows the stripping voltammetric profiles of the D/GCE towards various concentrations of Hg(II). The peak current increased when the Hg(II) concentration increased. Figure 4B shows the plots of current response towards concentration. A linear relationship was observed for Hg(II) from 0.1 to 100 µg/L. The limit of detection was calculated to be 17 ng/L based on a signal to noise ratio of 3. Table 1 shows the analytical method and analytical properties of several Hg(II) electrochemical sensors found in the literature. It is obvious that the proposed method showed wider linear ranges and lower detection limits than those from the literature.

To test and verify the accuracy and feasibility of the method, ten individually prepared D/GCE electrodes were used to carry out repetitive detection experiments on a Hg(II) solution. The peak current value was observed, and the relative standard deviation was calculated to be 4.2%, indicating that the electrode had good repeatability for Hg(II) detection. The results confirmed that D/GCE could be used as a good sensor for detecting Hg(II).

In the presence of bisphenol, hydroquinone, catechol, resorcinol, p-chlorophenol, K^+, Cu^{2+}, Ca^+, Fe^{3+}, Pb^{2+}, Mg^{2+}, Al^{3+}, Br^-, NO_3^-, and SO_4^{2-} at concentrations 5 times higher than that of Hg(II), the results showed that the presence of these substances did not interfere with the detection of Hg(II).

To verify the applicability of the method, the sensor was used in real samples. Hg(II) was added to tap water samples, and D/GCE was used to determine the samples in parallel 5 times. According to the test results in Table 2, the proposed sensor showed an excellent recovery rate.

Table 2. Tap water sample analysis of Hg(II) concentration using D/GCE.

Sample	Detection (μg/L)	Added (μg/L)	Found (μg/L)	Recovery (%)
1	0	10.00	10.17	101.70
2	0	20.00	21.81	109.05
3	0	30.00	31.23	104.10

4. CONCLUSION

In this paper, an electrochemical sensor based on a dithizone-modified electrode was prepared, and electrochemical detection of Hg(II) was conducted under a three-electrode system. Dithizone modification has excellent electrocatalytic and electronic properties, which can catalyse the Hg(II) redox. Under the best conditions, the proposed sensor could linearly detect mercury ions from 0.1 to 100 μg/L, and the detection limit can reach 17 ng/L.

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